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WADC TECHNICAL REPORT 55-84

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**PACKAGE SAFETY TEST
FOR
VOLATILE CORROSION INHIBITORS**

R. K. JOHNSTON

J. G. SCHAFER

L. D. McBETH

NOX-RUST CHEMICAL CORPORATION

JUNE 1955

WRIGHT AIR DEVELOPMENT CENTER

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MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2119
PROJECT No. 7312

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the Nox-Rust Chemical Corporation under Air Force Contract No. AF 33-(616)-2119. The contract was initiated under Project No. 7312, "Finishes and Materials Preservation", Task No. 73122, "Corrosion and Corrosion Prevention", formerly RDO No. 611-13, "Corrosion and Corrosion Prevention", and was administered under the direction of the Materials Laboratory, Protective Processes Branch, Wright Air Development Center, With Lt. O. R. Cunningham and Lt. A. H. Pagano acting as project engineers.

The cooperation of the following in supplying samples and analytical methods is gratefully acknowledged:

Angier Corporation, Framingham, Mass.
Central Ohio Paper Company, Detroit, Michigan
Cromwell Paper Company, Chicago, Illinois

This report covers work conducted from June 1953 to December 1954.

ABSTRACT

When a package is assembled using volatile corrosion inhibitors to protect ferrous metal components, there is no known method at present to indicate when the protection drops below a safe level. The development of such package safety tests, which can be applied without opening and re-packaging, was the major objective of this contract. All tests were conducted by personnel of the Nox-Rust Chemical Corporation at their laboratories. The development was carried through the laboratory stage, and resulted in two alternate methods, both based on a rust-inhibition test of the package atmosphere. Various limits of applicability of the two methods have been determined in laboratory tests. These methods are recommended for further study in application to actual packaging operations. Differences in the apparent mode of action of currently available volatile corrosion inhibitors have become apparent during the course of the laboratory work; and it is recommended that fundamental studies be made to determine the mechanisms involved.

PUBLICATION REVIEW

This report has been reviewed and is approved.
FOR THE COMMANDER.

WADC TR 55-84

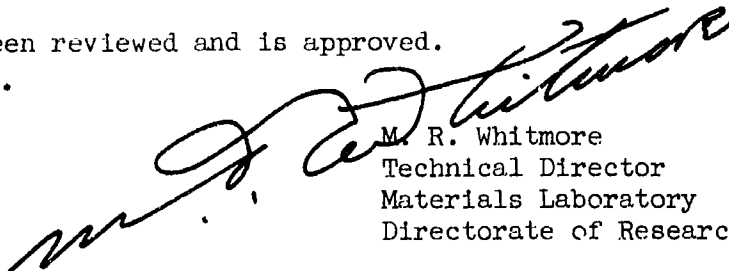

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INTRODUCTION

The use of volatile corrosion inhibitors in packaging has become an important method of rust prevention in the past five years. Although unknown prior to World War II, VCI materials today are used in a significant portion of in-package protective applications.

For the purpose of this report, volatile corrosion inhibitors (VCI's) are defined as solid or liquid materials which will prevent rusting of ferrous metal surfaces without direct application. This definition excludes all types of coatings, but includes any material which produces a rust-inhibitive atmosphere or which will migrate through the atmosphere and deposit rust-inhibitive films on ferrous metal surfaces. It might be more descriptive to call these materials "migratory rust inhibitors", but the term "VCI" has become widely accepted. To date no VCI's are known which offer general protection to non-ferrous metals.

The principal methods of application of VCI materials have been by impregnation into or coating upon paper products. Specification MIL-P-3420 has been written to cover VCI papers; and such materials have been used widely in military and industrial packaging.

One of the principal obstacles to wider acceptance of MIL-P-3420 materials for long-term packaging by the military has been the lack of any generally recognized method for determining just how long the package is safe. Under the present MIL-P-3420 specification, there is no answer to this question beyond the one year shed storage tests. Although future revisions of MIL-P-3420 probably will provide answers in terms of VCI exhaustion, it still would be desirable to have a method of testing for "safe" atmosphere in any specific package. In the present state of knowledge, VCI-packaged items which are critical as to rusting must be opened periodically for inspection and repackaged in fresh VCI material.

Performance testing of VCI materials has centered on short-term accelerated tests and on practical packaging tests; but neither of these approaches will give any information as to the condition of a package throughout its protective life. It is desirable to have a test which can be applied to a package at any time to show whether it is still safe with regard to rust protection without destroying the package. The initial development steps for such a "package safety test" are the subject of this report.

SECTION I

SCOPE OF CONTRACT

As outlined in Contract AF 33(616)-2119, it is desired to develop a practical method for indicating package safety with regard to steel surfaces and VCI materials. Such a method should show the point at which the best available inhibitors become inadequate. To be completely satisfactory, such a method must be operable without opening the package. It must be reliable under wide temperature and humidity ranges, and over extended periods of storage time. It should be applicable to all presently qualified MIL-P-3420 materials, and preferably to all available VCI powders and to VCI materials developed in the future. The method should be simple in design for use by non-technical personnel, and it should be easy to incorporate in various packaging methods.

Possible approaches to the development of such a package safety test can be classified as "direct" or "indirect". For "direct" methods, it is necessary to find some means of chemically or physically analyzing the package atmosphere to determine quantitatively the amount of inhibitor. For "indirect" methods, it is necessary to set up conditions to determine whether rust will form on some sort of activated ferrous surface.

The work toward the objectives of this contract has been divided into three phases, namely:

Phase I - literature survey

Phase II - investigation of direct and indirect methods

Phase III - evaluation of methods developed

It has been found possible within the scope of the contract to investigate only the "indirect" methods, for reasons described in Section III.

As to evaluation of methods (phase III), the laboratory work has been concerned with a study of "indirect" methods under various conditions of humidity, activation times, and package sizes. This has been entirely laboratory work; that is, it has not been extended to practical packaging. Such field packaging tests are outside the scope of this contract, but will be the final criterion as to whether the methods developed herein are workable.

SECTION II

LITERATURE SURVEY

As a guide to development of possible methods for package safety tests, it is necessary to define the classes of materials to be considered as VCI's. From a preliminary search of the literature, and from previous knowledge of the field, it is evident that the principal classes to be considered at present are amine nitrites, amine carboxylates, amine carbonates, and inorganic nitrites plus urea or other compounds containing the amide (CONH_2) group. The use of these materials as disclosed in patents and publications has been summarized in Rock Island Arsenal's Technical Report No. 53-3712, "Volatile Corrosion Inhibitor Bibliography", under date of 23 September 1953. Their search appears to be complete up to publication dates of about January or February 1953. Therefore, this work has not been duplicated here. The bibliography attached herewith consists of references not included in the Rock Island bibliography, plus selected references on special corrosion topics of interest in development of the package safety test.

It will be noted in later sections of this report that little direct use has been made of the literature survey, since most of the experimental techniques employed here have been developed empirically. The background literature as represented by Rock Island's bibliography and that attached herewith would be of more value as a starting point for any future work in "direct" methods of determining package safety, or in the use of electrical methods for detecting corrosion.

SECTION III

POSSIBLE METHODS FOR PACKAGE SAFETY TESTS

From the patent literature and from general knowledge of the VCI field, the principal classes of compounds used as VCI's are the following:

- (a) Amine nitrites
- (b) Inorganic nitrites plus urea or related compounds
- (c) Amine carboxylates
- (d) Amine carbonates

In looking at the possibility of developing a direct chemical method for analyzing atmospheres for VCI content, it became evident that a rather wide variety of materials are involved. Even when considering only VCI materials presently qualified under MIL-P-3420, the list will include a variety of amines, coupled with such acids as nitrous, caprylic, or benzoic. In addition, there are products resulting from reaction among the components of complex inhibitor mixtures, which may in themselves be VCI materials and in any case are poorly defined as to composition. These considerations rule out the possibility of a direct chemical analysis of the atmosphere as a practical package safety test which is applicable to all presently qualified materials. In addition to these considerations, it is recognized that new qualified VCI's under MIL-P-3420 would introduce additional problems in analysis.

Apart from methods of chemical analysis, the only other possible "direct" approach to the problem would involve complete elucidation of the mechanism by which VCI materials can prevent rust. This will not necessarily, nor even probably be the same for all VCI materials. Once such an understanding of mechanism is attained, it is possible in principle to devise some physical or chemical test for any package atmosphere which will determine whether this mechanism is operative. This line of reasoning leads directly to the consideration of the so-called "indirect" approaches, wherein the test applied to the atmosphere is actually a rust-inhibition test. Such test methods can be developed empirically without positive proof of mechanism. Although this approach is not attractive from the standpoint of obtaining fundamental information, it has been considered most likely to satisfy the requirement for a practical package safety test to be developed soon enough to be of value. Therefore, all laboratory work has been directed along the "indirect" approach, using rust-inhibition tests on package atmospheres.

For any such rust-inhibition tests, a specimen must be provided which is more susceptible to rusting than any packaged component. This susceptibility may be inherent in the specimen, or it may be induced temporarily by some sort of activation.

Some consideration was given to the use of an inherently rust-susceptible specimen to be included in the package, which could be observed periodically for rust. Such inherent susceptibility could be achieved by the use of a readily-corroded ferrous specimen, coupled with some lower-potential metal such as copper or brass. This system has two loopholes. First, it is impossible to say exactly what sort of specimen assembly will be more rust-susceptible than any possible packaged assembly. Second, the non-appearance of rust on the specimen would not be a criterion of safe VCI level

in a package; it might merely indicate good dry storage conditions up to the time of observation.

For temporary activation of a steel specimen, the most obvious and probably the most satisfactory method is by condensing moisture on it. The specimen itself should have a surface and composition such that rapid and definite rusting is obtained under condensation conditions. Much of the laboratory work performed under this contract has been concerned with establishing test conditions which will detect rapidly a non-inhibitive atmosphere, and will demonstrate inhibition in packages freshly assembled with currently qualified MIL-P-3420 materials.

There are probably methods of specimen activation, other than condensation of moisture, which would be applicable to package safety tests. No consideration has been given to such methods, in view of the positive results provided by the condensation procedure. The use of condensed moisture in the test may be open to the objection that it is too specific, and will not serve as a guide to rust inhibition under non-condensing conditions. However, the use of condensed moisture certainly does represent one of the most severe rusting conditions that a steel surface will encounter in normal packaging. It is felt that the method is justifiable on that basis and on the grounds of simplicity and rapidity.

It is possible to locate test specimens inside the package or in a separate test cell, inducing condensation on them in either case. The advantages and disadvantages of these two locations will be discussed in some detail in later sections of this report. Some thought has been given as to the difficulty of observing rust on internally-located test specimens; and possible methods of detecting rust by electrical measurements have been examined.

Experimental work in test development has proceeded along the lines outlined here; and is presented in approximately chronological order in Sections V to IX, inclusive.

SECTION IV

VCI MATERIALS USED

The immediate function of a "package safety test" would be its application to VCI papers qualified under MIL-P-3420. Therefore, these papers were used as the principal basis for test development. Samples of single-ply MIL-P-3420 papers were supplied by the following manufacturers:

Angier Corporation
Central Ohio Paper Company
Cromwell Paper Company
Ncx-Rust Chemical Corporation

It is believed that the samples thus supplied are representative of all types of inhibitors currently used in qualified MIL-P-3420 papers. These manufacturers also supplied weight loading methods and values on their papers. These methods are not necessarily those recommended by the respective manufacturers for official use under MIL-P-3420. The original reason for requesting the methods and test results was the need for such information in developing any direct method of analysis as a package safety test. It soon became evident that only a fundamental study of mechanism for all inhibitors involved, with full knowledge of their chemical composition, could be expected to lead to development of direct methods. Since such a study appeared to be outside the scope of this contract, it was not attempted. No use was made of the analytical methods supplied, except in two instances to check the manufacturer's figure on weight loading because of a discrepancy in performance.

In addition to the MIL-P-3420 papers, three samples of VCI powders were used for some of the test development work. These are commercially available materials, and were obtained on the market rather than directly from the manufacturers.

The following code system has been used to identify VCI materials used throughout this report:

<u>Code</u>	<u>Type of Material</u>
(a)	MIL-P-3420 paper, single ply
(b)	"
(c)	"
(d)	"
(e)	"
(f)	VCI Powder
(g)	"
(h)	"

Paper (e) is a 60 lb basis weight material; the others are 30 to 40 lb basis weight.

At the time these VCI materials were chosen, they were representative of the entire commercial field, so far as known. Since that time, it is quite probable that new classes of inhibitors are being used; and in any future work consideration should be given to adding to the list.

SECTION V

METHODS OF DETECTING INITIAL RUST

For a test specimen sealed inside a package, it would be desirable to have some method of detecting initial rust without direct visual observation. There appeared to be some promise in various methods of electrical measurement, as evidenced by numerous references in the literature. (28-45) One method of measuring the degree of corrosion was given by Hudson (28), involving the change in resistance of fine wires; this work was done with non-ferrous metals. To study the application of resistance measurements to the detection of initial rusting, a limited amount of laboratory work was performed here.

Experimental. Black iron wire and strip were obtained without any information as to composition. Each was the finest gauge readily obtainable. The wire was #36 gauge (0.005"), and the strip was 0.008" x 0.313". The resistances of coils consisting of various lengths of these materials were measured. The coils were immersed in 40% phosphoric acid and then allowed to rust in the atmosphere. The measured resistances were as shown in Table I:

TABLE I
RESISTANCE MEASUREMENTS

Material	Length	Resistance, Ohms		
		Before Cleaning	After Cleaning	After Rusting
Strip	32"	0.075	0.078	-----
Wire	80"	7.67	7.75	7.76
"	132"	11.13	11.21	11.20
"	88"	7.91	8.03	7.97
"	180"	15.27	15.43	15.40

Note: The rusting period used in the above tests varied from 10 minutes up to one hour, and in all cases resulted in fairly heavy visible rusting.

It can be seen from the above data that there was little significant change in resistance of the wire upon rusting. It seems reasonable that large changes in resistance would not occur until corrosion had penetrated to a considerable depth, and that therefore the method is not adaptable to the detection of initial rust formation.

To obtain a more sensitive measure of surface condition, it is necessary to measure the resistance of the surface itself. This can be done by determining the resistance of a contact between two parallel steel plates.

Experimental. Two steel plates, SAE 1010, dimensions 1-1/4" x 2" x 1/4", were mounted in a rig holding one plate stationary while the other plate was parallel to it, but movable in a perpendicular direction by means of a screw clamp, allowing the two plates to make contact without any shearing action. The contact pressure was not controlled accurately, but could be reproduced fairly well by hand tightening after some experimentation (using constancy of contact resistance as a criterion).

The steel plates were ground flat and finished with #240 aluminum oxide cloth prior to assembly. The contact resistance was measured by means of a Wheatstone bridge.

The plates were then separated, and rust was induced on their surfaces by chilling the whole assembly in a deep freeze and then moving it back into the laboratory atmosphere. The plates were then brought into contact again, and the resistance measured. The following data were obtained.

Clean contact	0.022 ohms
After one condensation	0.062 ohms
After two condensations	0.088 ohms

These figures are not corrected for the resistance of the lead wires.

From these data, it is evident that the increase in contact resistance upon rusting is definite and measurable, even by the relatively crude technique employed here. It appears quite possible to refine the system to make it sensitive to very small amounts of rust. However, it would then suffer from the practical disadvantages of being rather unwieldy, expensive, and difficult for untrained personnel to operate successfully as a package safety test. It would be necessary to mount the entire rig inside a package, operate it from outside, and provide some cooling method to cause condensation on the specimens. Another more fundamental disadvantage is that contamination of the contact surfaces by dust, grease, or condensed VCI chemicals would introduce large errors in the measured resistances. Thus, if the contact specimens were mounted in the test package with their surfaces apart, then rust or any other sort of surface contamination would show an increase in the resistance measured after closing the contacts.

Because of these limitations, the contact resistance method of detecting rust was not investigated further.

For externally located specimens, direct observation is the most practical method of detecting rust. For internal specimens, there was some question as to whether it is practical to design a view window in test packages for visual examination. However, it was the opinion of WADC personnel coordinating this development program that it would be feasible to include such view windows, and that further development should proceed on that assumption. Accordingly, all subsequent work was based on visual examination for the detection of initial rust formation.

SECTION VI

SPECIMEN COMPOSITION AND SURFACE FINISH

In selecting the proper type of specimen for tests of rust inhibition by VCI atmospheres, it is obviously desirable to look for a composition and surface finish that will be highly susceptible to rusting, in order that specimen inhibition can be used as a criterion of package safety. There is in the literature a considerable discussion of steel composition and finish as they affect corrosion rates, but little or no specific information on the effect of these factors on the time required for rusting to start. About the only basic principle gleaned from the literature was that certain inclusions in steel tend to make it more susceptible to initial rusting. The following excerpt illustrates: (Hudson, (21), page 247)

"The general conclusion reached by Homar was that under his experimental conditions there was a connection between the initial rust centers and positions of inclusions in the steel. In several solutions rusting always began at a number of sulphide inclusions or at particles of rolled-in iron oxide scale. Strangely enough, only a small portion of the sulphide inclusions acted in this way. Other types of inclusions such as alumina, silicates, appeared to be inert."

This passage refers to corrosion in solution rather than to atmospheric rusting; but the conclusions should be valid for atmospheric rusting under condensation conditions.

Various types of steel were considered for use as test specimens, but due to considerations of availability the following were selected for experimental work:

TABLE 2

COMPOSITION LIMITS OF STEEL SPECIMENS

SAE#	Type	Principal	Non-Ferrous	Constituents, %	
		C	S	Mn	P
1018	Low Carbon	0.15-0.20	0.05 Max.	0.60-0.90	0.04 Max.
1095	High Carbon	0.90-1.05	0.05 Max.	0.30-0.50	0.04 Max.
1113	High Sulfur	0.08-0.13	0.24-0.33	0.70-1.00	0.07-0.12

It is believed that these are representative of steels used widely in fabrication of parts and assemblies requiring package protection. Further, the 1113 high-sulfur steel has the reputation of being extremely susceptible to rusting compared to low-sulfur steels, so it is of interest as a specimen material.

Experimental. Specimens were cut from 1095 and 1113 bar stock, of the following sizes:

1095 - 1" x 1/2" x 1-1/4"

1113 - 1" x 1" x 1-1/2"

Each was drilled lengthwise with a 3/16" hole, through which was inserted a 1/8" copper tube for ice water circulation.

The four "test surfaces" (undrilled) were finished on a portable sander using aluminum oxide belts of various grits.

Moisture was condensed on the test surfaces by pumping ice water through the copper tubing. The specimens were in the laboratory atmosphere at 80-86 F. and 35-45% relative humidity.

Ice water circulation was continued for 5 to 9 minutes, and then the specimens were allowed to warm up and dry off without assistance. The test was considered complete at this time, and observations of rusting were made as shown in Table 3.

TABLE 3
EFFECT OF COMPOSITION AND SURFACE ON RUSTING

Steel	Grind	Schedule, Minutes		Total Warmup Period	Type	% Rust*
		First Cond. at	Total Cooling Period			
1113	24	2	5	16	Very heavy	---
"	80	2	5	16	Heavy	---
"	180	2	5	16	Medium	---
"	320	2	5	16	Fine	---
1095	24	2	5	15	Fine	20%
"	80	2	5	15	Fine	15%
"	180	2	5	15	Fine	15%
"	320	2	5	15	Fine	3%
1095	24	3	9	24	----	25%
"	80	3	9	24	Fine	25%
"	180	3	9	24	Stain	25%
"	320	3	9	24	Stain	3%

* So-called "consolidated" percentage ratings, assuming that all rust is consolidated and calculated as percent of total specimen area. In all cases the actual rust was well distributed over the specimen.

These data confirmed the susceptibility of 1113 high-sulfur steel to rusting. Further, they indicated that very definite observable rusting could be obtained in relatively short periods by condensing moisture on the specimen surfaces. The finer grinds appeared less suitable because of lighter rusting. The very coarse #24 grind showed the heaviest rusting in all cases, but is somewhat unsuitable because of irregularity. Of the grinds tested here, the #80 appeared the most suitable. Later it was observed that specimens ground with #120 grit would rust just as fast as those ground with #80; and the #120 grind was more free of irregularities which can cause erratic rusting. Therefore, #120 aluminum oxide cloth was used for all subsequent test work.

SECTION VII

RUST INHIBITION TEST DEVELOPMENT

In developing a package safety test based on determination of rust-inhibiting properties of the package atmosphere, a great many variables were explored. Certain aspects of test technique were common to almost all of the experimentation described in this section, so they will be summarized here:

Specimen. For most of the work a round steel bar $3/8$ " x 4" was used as the test specimen. Finishing was accomplished by rotating the bar at about 300 RPM in a drill chuck while applying the proper aluminum oxide abrasive cloth by hand. Coarse abrasive cloth (#50) was needed for preliminary finishing; and it was found advantageous to use a portable electric sander with #50 cloth belts to speed up this grinding. Final finishing was done with #120 aluminum oxide cloth. The electric sander was used for final finishing in earlier work; later it was recognized that metal overheating could occur by this method; and hand application of the abrasive cloth to the rotating specimen was used for all subsequent finishing. One end of the specimen was left unfinished except for the removal of superficial rust and scale; the other end of the specimen was well rounded using coarse abrasive, and then finished with #120 abrasive in the same manner as the lateral surfaces.

No elaborate degreasing procedures were used in most cases, since they were found to be unnecessary. Preliminary degreasing in naphtha was used; and the usual precautions in avoiding subsequent surface contamination were observed, particularly with regard to fingerprint contamination. Treatment after grinding consisted only of removing superficial dust by wiping with gauze.

When other shapes or forms of specimens were used, finishing procedures were similar to those described above. The compositions used were SAE 1018 or 1113 in all cases where steel rod was used.

Package and test cell. In most of the test development work one-gallon glass jars with three-inch openings were used as "packages." The jars were lined with the VCI paper under test, and the jar mouths were closed with rubber stoppers carrying any necessary connections. In some of the tests the specimen was mounted inside the "package;" this arrangement is known as an "internal test cell." In other tests the specimen was mounted in an "external test cell," of various designs and sizes. When an external test cell was used, it was necessary to circulate the air between the "package" and the cell. This was done by means of a White Mist Air pump, Model #50, made by the Haddaway Manufacturing Company. This pump is rated at 50 cubic inches of air per minute against 1-1/2 psi back pressure; and it has been found to deliver 80 cubic inches per minute with free discharge. There is little variation among different pumps in delivery rate. The pumps were modified by putting on an air inlet connection to permit recirculation of air through the "package" and test cell.

Temperature and humidity regulation. All of this work was done at package temperatures of 25°C., thus avoiding the criticism of much work on VCI testing that has involved abnormally high temperatures. For humidity regulation, it would have been most desirable to carry out all operations in

a room maintained at the test humidity. However, it was impossible to operate the constant humidity room at relative humidities other than 50%, owing to the use of the room for other test work. Therefore, most of the work described in this report was performed using constant humidity solutions in the test apparatus. In most cases the constant humidity solutions were placed in the "packages", but in other test work the constant humidity solutions were used in external test cells. For all early work saturated salt solutions were used to control humidity, as listed in Table 4:

TABLE 4
HUMIDITY CONTROL SOLUTIONS

R.H., %		Saturated Salt Solution
Actual	Nominal at 25°C.	
10 at 20°C	10	Zinc chloride
20 at 20°C	20	Potassium acetate
31 at 24.5°C	30	Calcium chloride
42 at 20°C	40	Zinc nitrate
51 at 24.5°C	50	Calcium nitrate
58 at 20°C	60	Sodium bromide
71 at 25°C	70	Ammonium chloride and potassium nitrate
79.3 at 25°C	80	Ammonium chloride
90 at 20°C	90	Zinc sulfate

All of these humidity values have been rounded off to the nearest 10% for simplicity in discussion, since it was not felt that the accuracy of the humidity controls justified reporting the values any closer. Some of these salts are open to question as to the possible effects on rust inhibition and on VCI chemicals in the atmosphere. However, preliminary checks indicated no observable effects; and the solutions were used. For later work, a series of glycerin-water solutions were used to maintain constant humidity; and this method is to be preferred.

Results. The experimental data obtained in this preliminary test development work are summarized in Tables 5-16.

Static Jar Tests. The first static jar tests, using SAE-1113 steel specimens, are described in Table 5. It will be noted that these are "internal specimen" tests, with static equilibration. The paper/volume ratio was 5.8 ft²/ft³. Condensation was formed on the specimens by pumping ice water through them. It is seen from the results that VCI paper (d) protects 1113 steel at 50 or 70% R.H., whereas papers (b) and (e) will not--at least up to 72 hours equilibration. Papers (a) and (c) were not available at the time these tests were run.

To investigate more thoroughly the conditions for protection of SAE-1113 steel by VCI paper (b), the series of tests listed in Table 6 was run. It was found that complete protection could not be obtained, even using static equilibration for up to 504 hours at 25°C. Circulating the air through the package during equilibration did not appear to help matters nor did equilibration at temperatures up to 66°C. The difficulty appears to be inherent in the VCI itself, rather than in the particular paper sample. A check on the inhibitor weight loading by the manufacturer's method showed the proper amount of

TABLE 5

STATIC JAR TESTS, SAE-1113 SPECIMENS

Test No. 23-28

Temperature: 25°C

Humidity: 50-70%

Specimen: SAE-1113 steel rod, 5/8" x 1", drilled lengthwise and tapped for copper tubing fittings. Finished with #120 aluminum oxide cloth, on entire curved surface.

Package: One-gallon glass jar.

VCI Material: Paper 7" x 16" lining jar. Paper/volume = 5.8 ft²/ft³.

Specimen Location: Suspended in jar about 2" from top by means of copper tubing.

Equilibration: Static; specimen in place; time and humidity as shown. Humidity maintained by saturated salt solution in beaker in bottom of jar.

Condensation: By pumping ice water through specimen for 10 minutes. Rust observations after specimen warmup.

VCI Paper Used	R.H. %*	Equilibration Time, Hours		
		24	48	72
(b)	50	Very heavy rust overall	Very heavy rust overall	Very heavy rust overall
(b)	70	" "	" "	" "
(d)	50	No rust	No rust	No rust
(d)	70	No rust	No rust	No rust
(e)	50	Light rust overall	Light rust overall	Very light rust overall
None	50	Fine rust overall	-----	-----
None	70	Large rust spots overall	-----	-----

* 50% maintained with saturated calcium nitrate.

70% maintained with saturated ammonium chloride and potassium nitrate.

TABLE 6

STATIC AND DYNAMIC JAR TESTS
VCI Paper (b), SAE-1113 Specimens

Test No. 23-29 to 23-33

Temperature: As shown

Humidity: 50-70%

Specimen: SAE-1113 steel as in Table 5

Assembly: As in Table 5

Equilibration: As shown below

Condensation: By pumping ice water through specimen for 10 minutes.
Rust observations after warmup of specimen.

VCI Paper Used	RH*	Equilibration Procedure**	Rusting
(b)	50%	72 hours at 25°C. without specimen; then 4 hours at 46°C. with specimen.	Large spots lower half
(b)	70%	72 hours at 25°C. without specimen; then 24 hours at 46°C. with specimen.	Large spots overall
(b)	70%	72 hours at 25°C. without specimen; then 26 hours at 46°C. with specimen.	Large spots overall
(b)	50%	72 hours at 25°C. without specimen; then 24 hours at 46°C. with specimen; then 24 hours at 66°C. with specimen.	Large spots overall
(b)	50%	72 hours at 25°C. without specimen; then 192 hours at 25°C. with specimen.	Light rust overall
(b)	70%	72 hours at 25°C. without specimen; then 432 hours at 25°C. with specimen.	Light rust overall
(b)	50%	2 hours circulating (80 in ³ /min) at 25°C. with specimen.	Heavy rust overall
(b)***	50%	18 hours circulating (80 in ³ /min) at 25°C. with specimen.	Light rust overall
(b)***	50%	72 hours circulating (80 in ³ /min) at 25°C. with specimen.	Light rust overall
(b)***	50%	72 hours static at 25°C. with specimen	Light rust overall

* 50% maintained with saturated calcium nitrate.
70% maintained with saturated ammonium chloride and potassium nitrate.

** All equilibrations static except as noted. At the higher temperatures, no change was made in the humidity solution; therefore humidities at these higher temperatures are much lower than nominal values shown. All air circulations at 80 in³/minute, pumping from top to bottom of jar.

*** Laboratory-impregnated paper from solid inhibitor; 2 g/ft².

inhibitor; and protection tests using laboratory-impregnated papers showed similar results to those on the manufacturer's sample. It is possible that the high-temperature data do not reflect a true picture of performance, since the presence of the constant-humidity solution throughout equilibration would cause condensation on the specimens at the times of raising the temperature of the assembly. The use of warming procedures at the time of packaging in order to promote volatilization of VCI chemicals has been recommended by Baker (2). It is evident that this must be done under dry conditions, or the net result might be to cause condensation of moisture on the slower-warming metal parts within the package.

To study further the effect of specimen composition and equilibration time, the data of Table 7 were obtained. The VCI papers were shown to vary widely in the static equilibration time required for protection. Also, it was shown that 1018 steel can be protected within a practical equilibration time, whereas the 1113 steel cannot be so protected by (b) or (c). The following minimum equilibration times (to obtain protection) illustrate this point:

<u>VCI Paper</u>	<u>SAE-1113</u>	<u>SAE-1018</u>
(a)	7 hours	Less than 4 hours
(b)	More than 72 hours*	72 hours
(c)	More than 96 hours*	72 hours
(d)	1/4 hour	1/4 hour
(e)	96 hours	72 hours

* Longer equilibrations not run in this series.

To study further the relative difficulty of protecting 1113 steel, a series of MIL-P-3420 dynamic tests was run as recorded in Table 8. It was evident that only the (d) and (e) papers gave complete or near-complete inhibition of 1113 steel in this type of test. Using the regular SAE-1045 specimen per MIL-P-3420, the (b) paper was found to give results interpreted as passing. The (c) paper, which was tested much later, failed badly with regular specimen. This will be discussed in more detail in connection with Table 16. The other papers were not tested with regular MIL-P-3420 specimens.

The difficulty of protecting 1113 steel by certain VCI papers, in a variety of test procedures, prevents the use of this steel as a specimen for a package safety test. There is a need for determining the limits of applicability of all VCI papers to various ferrous compositions; but such a study is outside the scope of this contract.

VCI Powders. Evaluation of three commercially available VCI powders was carried out using the static jar test described previously. All of this work was done at 25°C. and 50% R.H., using SAE-1018 steel specimens. The results listed in Table 9 indicated that the (f) powder gave protection without requiring any equilibration time. The (g) required about 10 minutes. Both of these materials were effective at 1 gram per cubic foot. The (h) did not build up an inhibitive atmosphere even within 14 days when using 11.2 grams per cubic foot; and it required somewhere between 4 and 16 hours when using 37.5 grams per cubic foot.

This preliminary work on VCI powders was not carried further, but serves to indicate that the internal-specimen methods are applicable to VCI powders as well as to papers.

TABLE 7

STATIC JAR TESTS, SAE-1113 AND 1018 SPECIMENS

Test No.: 23-36, 23-37, 23-40, 23-43

Temperature: 25°C

Humidity: 50%

Specimen: Steel rod, SAE-1113 or 1018, 5/8" x 1", drilled lengthwise and tapped for copper tubing fittings. Finished with #120 aluminum oxide cloth, on entire curved surface.

Assembly: As in Table 5

Equilibration: Static; specimen in place; 50% R.H. maintained by saturated calcium nitrate solution in beaker in bottom of jar.

Condensation: By pumping ice water through specimen for 10 minutes. Rust observations after specimen warmup.

Specimen Rusting with Following

Equil. Time, Hrs.	VCI Papers:					
	(a)	(B)	(c)	(d)	(e)	None
<u>SAE-1113 Specimens</u>						
1/4	----	----	----	None	----	----
1/2	----	----	----	None	----	----
4	Spots	----	----	None	----	----
7	None	----	----	----	----	----
17	----	----	Heavy	None	----	----
24	None	----	----	----	Lt.spotty	----
48	None	Medium	Medium	----	Heavy	----
72	None	Light	Medium	----	Lt.stain	Medium
96	----	----	Light	----	None	----
<u>SAE-1018 Specimens</u>						
1/4	----	----	----	None	----	----
1/2	----	----	----	None	----	----
4	None	----	----	None	----	----
7	None	----	----	----	----	----
17	----	----	Medium	None	----	----
24	None	Light	----	----	Lt.spotty	----
48	None	Spots*	Spots*	----	Few spots*	----
72	None	None	None	----	None	V.light
96	----	None	----	----	----	----

* Duplicate test showed no rust

Note: All of above tests were run in duplicate, and each pair gave identical results except in the three tests noted.

When rust was observed, it was uniform over the specimens except as noted in table.

TABLE 8

DYNAMIC TESTS PER MIL-P-3420

Test No. 23-31 and 23-44

VCI Paper	Specimens	Rusting on Specimens		
		Blank	Vapor	Contact
(b)	SAE-1045 (MIL-P-3420)	80% edge rust; 15 spots in center	One spot*	One spot*
(a)	SAE-1113	100% heavy	10%	None
(b)	SAE-1113	100% heavy	65% heavy	Stain
(c)	SAE-1113	100% heavy	80% heavy	One spot
(d)	SAE-1113	100% heavy	Stain	Stain
(e)	SAE-1113	80% heavy	One spot	None
(c)	SAE-1045 (MIL-P-3420)	40%	60%	None

* Appeared to be derived from some sort of deposition; not necessarily interpreted as failing to ..

TABLE 9

VCI POWDERS
STATIC JAR TESTS

Test No. 23-49, 23-50, 23-51

Temperature: 25°C

Humidity: 50%

Specimen: SAE-1018 steel rod, 5/8" x 1", drilled lengthwise and tapped for copper tubing fittings. Finished with #120 aluminum oxide cloth on entire curved surface.

Package: One-gallon glass jar.

VCI Material: Powdered material, in open half-pint jar inside package.

Specimen Location: Suspended in jar about 2" from top by means of copper tubing.

Equilibration: Static; specimen in place; time as shown below. Humidity maintained at 50% with saturated calcium nitrate solution in bottom of jar.

Condensation: By pumping ice water through specimen for 10 minutes. Drying time 30 to 45 minutes; specimens observed afterward.

VCI			Equilibration Times (Individual Tests)	
Powder Used	Grams Used	g/ft ³	Tests Showing No Rust	Test Showing Rust
(f)	1.5	11.2	15,5,2,1,0 (Minutes)	-----
(f)	0.134	1.0	90,1 (Minutes)	-----
(g)	1.5	11.2	60,35 (Minutes)	-----
(g)	0.134	1.0	30,10,10 (Minutes)	10 (Minutes)
(h)	1.5	11.2	-----	5,15,30,35 (Minutes)
				16,48,72 (Hours)
				14 (Days)
(h)	5.0*	37.5	16 (Hours)	4 (Hours)

* Split between two half-pint jars.

External Test Cell Development. An external test cell would have the practical advantage of easy visual observation of test specimens, and simplified assembly so far as the package itself is concerned. The results of the first tests in this development are listed in Table 10. A 250-ml. Erlenmeyer flask was used as the test cell, with sidearms blown into the top and bottom (air inlet and outlet). The specimen was low-carbon seamless steel tubing, plugged at one end; condensation was induced by pouring ice water into the open end. In these tests, equilibration was at 30% R.H., circulating air between the package and cell. Then the cell was sealed off and remained static for several days. It was then adjusted to 50% R.H., after which condensation was induced on the specimen. The results indicated that none of the papers tested would give protection after 16 hours circulation and 65 hours sealoff before condensation. This long sealoff time was based on the theory that it would favor establishment of absorption equilibrium of the VCI chemicals on the steel surfaces. Evidently, however, the amount of VCI chemical transferred to the test cell and specimen during the 16 hours' circulation was not sufficient to inhibit rusting. With 65 hours of circulation and 65 hours sealoff before condensation, the (a) and (d) papers gave protection.

Further developments in the test methods are shown in Table 11. The results using air circulation during equilibration, and sealoff before condensation, again indicated that it was difficult to transfer enough chemical by this procedure. When circulating throughout equilibration and condensation, only the (d) paper gave complete protection.

Several variations were introduced in the third group of tests in Table 11, so the conclusions are not clear-cut. The (d) and (e) papers gave protection, whereas the (a), (b), and (c) did not. The improved protection of the (e) paper over previous tests may be a function of the lower relative humidity, or of the reduction in cell size.

The data shown in Table 12 were obtained with an external test cell assembly in approximately its final form, using a round bar as the specimen and inducing condensation by pouring coolant into a funnel fitted around the upper end of the specimen. The 45-ml. test cell was used; and there has been no subsequent change in this item. The small volume is desirable from the standpoint of minimum change in composition of the package atmosphere when connecting and circulating the cell.

It appeared desirable to consider the use of dry ice mixtures as coolants, in order to obtain condensation at low humidities. Using wet ice, condensation is theoretically unobtainable at package humidities below 19%. Practically speaking, adequate condensation cannot be induced in this type of test by wet ice at 30% R.H. or below. Therefore, wet ice appeared unusable at low humidities, since it had been demonstrated previously that cell sealoff and humidity adjustment to 50% resulted in failing tests - presumably due to inadequate amount of VCI available in the test cell.

In the tests shown in Table 12, dry ice-isopropanol was used as the coolant; and 50% R.H. was used, with air circulation continued throughout the condensation and warmup. The results for SAE-1113 specimens confirm the data of Table 7, showing that this high-sulfur steel is very hard to protect against rust, but that the (d) paper gives complete protection. (Note: In Table 7, the (a) paper also protected 1113 steel in static jar tests; in the Table 12 external-cell tests the (a) paper was not effective.) The data of Table 12 on SAE-1018 specimens are quite erratic for most of the papers, with the (d) paper again showing

TABLE 10

EXTERNAL TEST CELL DEVELOPMENT
EQUILIBRATION TIME STUDY

Test No. 23-42
Temperature: 25°C
Humidity: 30-50%

Specimen: Low-carbon seamless steel tubing, 21-gauge, 1/2" x 3-1/2".
Outside surface finished with #120 aluminum oxide cloth.

Package: One-gallon glass jar.

VCI Material: Paper 7" x 16" lining jar
Paper/volume = 5.8 ft²/ft³

Test Cell: 250 ml. Erlenmeyer flask, with sidearms top and bottom
(air inlet and outlet).

Specimen Location: In test cell, mounted in rubber stopper with 2" length of
specimen actually in cell. Bottom end of specimen plugged
with small rubber stopper.

Equilibration: Air recirculated at 80 in³/minute over specimen, from top
of package to top of test cell, holding 30% RH with calcium
chloride solution in package. Then test cell clamped off
and further equilibrated at 25°C. for periods as shown, No
humidity adjustment made until 1 hour before activation;
then 20 ml. saturated calcium nitrate solution added to test
cell without disturbing atmosphere, to bring to 50% R.H.

Condensation: By pouring ice water into top end of specimen. Rust ob-
servations after warmup.

Hours Recirc.	Hours Sealed	Specimen Rusting using Following VCI Papers			
		(a)	(b)	(d)	(e)
3	65	Very light	Light	Light	Light
5	89	Very light	Light	Very light	Very light
16	65	-----	Light	Very light	Very light
65	65	None	Very light	None	Few pinpoints

Table 11

EXTERNAL TEST CELL DEVELOPMENT
SEALOFF VS CIRCULATION

Test No.: 23-47, 23-48
 Temperature: 25°C
 Humidity: 30-50%

Specimen: Low-carbon steel tubing; see Table 9
 Package: One-gallon glass jar
 VCI Material: Paper 8" x 16" lining jar; paper/volume = 6.6ft.2/ft.3
 Test Cell: 250 or 500 ml. Erlenmeyer flask, or 45 ml. test tube.
 Each cell had sidearms at top (air inlet) and bottom (air outlet).
 Specimen Location: In test cell; see Table 10
 Equilibration: Air recirculated at 80 in 3/minute over specimen, from top of package to top of cell, holding specified humidity with proper saturated salt solution in package.
 Condensation: By pouring ice water into top end of specimen. Cell either sealed or circulating; if sealed, cell humidity was adjusted after sealing. Rust observations after specimen warmup.

VCI Paper	(a)	(b)	(c)	(d)	(e)
<u>First Set of Tests:</u>					
Cell Size, ml.	250	250	250	250	250
Equilibration	- - - -	72 hours circulating, 30% R. H. - - - -			
Activation	- - - -	Cell sealed; 50% R. H. - - - -			
Specimen Rusting	60%	75%	---	20%	40%
<u>Second Set of Tests:</u>					
Cell Size, ml.	250	250	250	250	250
Equilibration	- - - -	72 hours circulating, 50% R. H. - - - -			
Activation	- - - -	Circulation continued throughout; 50% R.H. - - - -			
Specimen Rusting	Light Spotty	Few Spots	Light Overall	None	Few Spots
<u>Third Set of Tests:</u>					
Cell Size, ml.	500	250	250	500	45
Equilibration	- - - -	72 hours circulating; 50% R. H. - - - -			
Activation	- - - -	Circulation continued throughout; 50% R.H. - - - -			
Specimen Rusting	10%	20%	50%	None	None

TABLE 12

EXTERNAL TEST CELL DEVELOPMENT
PRELIMINARY WORK ON DRY ICE COOLANT

Test No.: 23-56
Temperature: 25°C
Humidity: 50%

Specimen: Round steel bar, 3/8" x 4"; SAE 1018 or 1113.
Finished with #120 aluminum oxide cloth on test surfaces including one end, which was rounded.

Package: One-gallon glass jar.

VCI Material: Paper 8" x 18" lining jar.
Paper/volume = 7.5 ft²/ft³

Test Cell: 45 ml. test tube with sidearms at top (air inlet) and bottom (air outlet).

Specimen Location: In test cell in rubber stopper; 1 inch of specimen within cell. Funnel fitted around top end of specimen for coolant.

Equilibration: VCI paper equilibrated in package under static conditions for at least 72 hours, with saturated calcium nitrate solution for 50% R.H. Package then connected to test cell and air circulated at 80 in³/min over specimen for time shown below.

Condensation: By pouring dry ice-isopropanol into funnel; coolant left in funnel until warmup and evaporation of condensate occurred. Air circulation continued throughout.

Circulation

Time, Minutes	Specimen Rusting with Following VCI Papers:				
	(a)	(b)	(c)	(d)	(e)
SAE-1113 Specimens					
15	50%	25%	100%	None	50%
30	20%	10%	100%	None	5%
30	60%	20%	100%	None	20%
60	60%	5%	100%	None	5%
SAE-1018 Specimens					
15	80% H	1 spct	90% L	None	1 Spot
30	90% H	None	None	None	None
30	50% S	10% S	90% H	None	End only
60	90% H	20% S	100% S	None	20% S
60	90% H	None	S	None	S
90	H	S	S	None	S
120	H	L	S	None	S

Code for type of rusting:

L - light
H - heavy
S - spotty

complete inhibition.

At this point in the test development, due to the erratic results encountered on SAE-1018 specimens, a series of tests were run as blanks (no VCI paper), using external test cells and various humidities and cooling procedures, as summarized in Table 13. It became evident that adequate rusting of 1018 specimens in "blank" tests could not be obtained at package humidities of 30% or below, when circulating air throughout the condensation and warmup periods. This was true for a variety of conditions of coolant temperatures and time of application, and for varying lengths of exposed specimen. When well-packed mixtures of dry ice and isopropanol were used, the coolant temperature was about -70°C . This resulted in frost formation at all humidities down to and including 10%; but no rust formed in many of the tests. It appeared that no rust would form under freezing conditions; then as the bar warmed up the frost would either drop off, or else evaporate without melting. In either case, there is a chance of inadequate contact time of liquid water to give rusting.

Further blank tests are summarized in Table 14. The condensation technique adopted for these tests was the continuation of air circulation for 10 minutes after adding the dry ice-isopropanol. Then the cell was sealed off and left undisturbed until warmup was complete. The theory behind this procedure is that the 10 minutes' circulation, when testing VCI papers, will make available to the condensate a sufficient amount of VCI chemical to inhibit rust, provided the package atmosphere is still "safe". The subsequent sealing off of the test cell merely retards evaporation and raises the effective cell humidity, so as to permit rusting in tests with blank or "unsafe" atmospheres. The data of Table 14 demonstrated that rusting of blanks can be obtained under these conditions down to and including 10% R.H. In some cases there was a tendency for the rusting to be localized at the lower ends of the specimens due to rundown of the condensate. Therefore, it appeared more desirable to use a shorter length of the bar exposed in the cell to minimize such rundown. Tests using 1/2" exposed length, however, still showed this localized rust.

In attempting to apply this external test cell assembly to the VCI papers, it appears that at humidities of 50% or higher the most satisfactory coolant will be wet ice; and at 30% or lower, dry ice must be used. Initial tests on the VCI papers using the 10-minute cell sealoff procedure are listed in Table 15. These tests were run at 50% R.H., with wet ice coolant. The specimens were SAE-1018, and protruded into the test cell only about 1/4". In the first test, the papers were equilibrated in the "packages" under static conditions for 600 hours; then they were hooked to the test cells and circulated for 3-1/2 hours. Rusting was heavy when using the (a) or (c) paper, questionable on the (b) and (e) papers, and zero on the (d) paper. This behavior of the (a) and (c) papers is in marked contrast to the good tests obtained on 1018 steel with these papers in the static jar test (see Table 7).

Further external cell tests were run on the (b), (d), and (e) papers (Table 15) with 720 to 840 hours package equilibration, and varying times of specimen equilibration. It was found that about 6 hours of circulation was necessary for the (b) paper to establish inhibition in the external cell. Less than 15 minutes is required for (d); and short circulation times also appear sufficient for (e) although two of the tests were questionable as to rusting.

The discrepancy in results on the (a) and (c) papers indicated that possibly they operate by a different mechanism than the other papers. This was borne out somewhat, at least for paper (a), by the data shown in Table 16, in which both

Table 13

EXTERNAL TEST CELL DEVELOPMENT
BLANKS AT LOW HUMIDITIES

Test No.: 23-57, 23-58, 23-59

Temperature: 25°C

Humidity: 10-50%

Specimen: Round steel bar 3/8" x 4", SAE-1018. See Table 12
 Package: One-gallon glass jar
 VCI Material: None
 Test Cell: 45 ml. test tube as in Table 12
 Specimen Location: In test cell as in Table 12; length of specimen within cell was varied.
 Equilibration: Circulated 3 hours at 80 in³/minute to establish humidity using proper saturated salt solution in package.
 Condensation: Poured coolant into funnel. Nature of coolant and time of application varied as specified below. Air circulation continued throughout.

Coolant			Length of Specimen in Cell, Inches	Condensation and Rusting at Following Relative Humidities;				
Type	T°C	Time		10%	20%	30%	40%	50%
Ice	0-5	10 Min.	2-1/2	C: None	None	Haze	Haze	Heavy
				R: None	None	None	None	Medium
Ice	0-5	10 Min.	1	C: None	Haze	Light	Med.	Heavy
				R: None	None	None	None	Medium
Ice	0-5	Warmup*	1	C: None	None	Medium	Heavy	- - -
				R: None	None	None	None	
CO ₂	70	Warmup*	1	Frost formed at all humidities. Heavy rust on bottom end in all tests.				
CO ₂	-70	5 Min.	3/4	C: Frost	Frost	Frost	Frost	Medium
				R: Lt.**	Lt.**	None	Lt.**	Medium
CO ₂	-40	Warmup*	1-1/2	C: Haze	Med.	Good	Good	Good
				R: None	None	None	None	Medium
CO ₂	-70	5 Min.	1-1/4	C: Frost	Frost	Frost	Frost	Frost
				R: None	None	None	Trace	Lt.**
CO ₂	-40	45 Min.	1-1/4	C: Light	Fair	Fair	Good	Good
				R: None	None	Light	Spots	Spots

Note: At 45 minutes, when coolant was removed from funnel, the specimen in 10% RH was dry, the specimen in 20% RH was nearly dry, and others were wet.

* Coolant left in funnel until specimens were all dry.

** End of specimen only.

Table 14

EXTERNAL TEST CELL DEVELOPMENT
BLANKS AT LOW HUMIDITIES (CONT.)

Test No.: 23-60, 23-61

Temperature: 25°C

Humidity: 10-50%

Specimen: Round steel bar, 3/8" x 4", SAE-1018. See Table 12

VCI Material: None

Assembly and Equilibration: Same as in Table 12

Condensation: After pouring coolant into funnel, circulated for 10 minutes to cause condensation; then clamped off test cell to retard evaporation from specimen. Coolant was dry ice-isopropanol in all tests, at -60 to -70 C., and remained in the funnel until warmup; rust observations made afterward.

Length of
Specimen
in Cell,
Inches

Specimen Rusting at Following
Relative Humidities:

	10%	20%	30%	40%	50%
1-1/4"	Overall	Overall	Overall	Overall	Overall
1-1/4"	Light	Medium	Heavy	Heavy	Heavy
	overall	overall	overall	overall	overall
1-1/4"	Definite	Heavy	Heavy	Definite	Heavy
	near end	near end; spots on 50% of remainder	near end; spots on 80% remainder	overall	overall
1/2"	Heavy	Definite	Heavy	Heavy	Heavy
	near end; light overall	near end	near end	near end	near end

Table 15

EXTERNAL CELL METHOD
APPLICATION TO VCI PAPERS

Test No.: 23-62, 23-65, 23-66

Temperature: 25°C

Humidity: 50%

Specimen: Round steel bar, 3/8" x 4", SAE-1018. Lower end of bar polished with #120 aluminum oxide cloth and used as critical test surface.

Package: One-gallon glass jar

VCI Material: Paper 8" x 18", lining jar; paper /volume = 7.5 ft.²/ft.³

Test Cell: 45 ml. as in Table 12

Specimen Location: In test cell in rubber stopper, with bottom end of bar (critical test surface) barely protruding into test cell. Funnel fitted around top end of specimen for coolant.

Equilibration: Paper equilibrated under static conditions in package with calcium nitrate solution, for periods as indicated below. Then air circulated at 80 in 3 /minute through test cell (over specimen) for periods indicated.

Condensation: By pouring ice water into funnel. Air circulation continued for 10 minutes; then test cell clamped off and held until warmup.

Equilibration Time, Hours		Rusting on end of specimen with following VCI papers:				
Paper Only (Static)	With Specimen (Circulating)	(a)	(b)	(c)	(d)	(e)
600	3-1/2	Heavy	Lt. stain	V. Heavy	None	1 spot
720	1/4	- - - -	- - - -	- - - -	None	Trace
to	1/2	- - - -	- - - -	- - - -	None	Trace
840	1-1/2	- - - -	Heavy	- - - -	- - - -	- - - -
"	2	- - - -	Heavy	- - - -	- - - -	- - - -
"	6	- - - -	None	- - - -	- - - -	- - - -
"	16	- - - -	None	- - - -	- - - -	- - - -
48	1	- - - -	Few spots	- - - -	None	None
24	1	- - - -	20% light	- - - -	None	None
0	6-1/2	- - - -	Pass*	- - - -	None	Pass*

* One pinpoint

Table 16

VCI PAPERS (a) AND (c)
VARIOUS TEST METHODS

Test No.: 23-63, 23-64, 23-67, 23-68, 23-72, 23-81

External cell tests per Table 11. Humidity 50%

Internal specimen (static jar) tests per Table 5 with following changes:

Humidity 50%

Paper 8" x 18"; paper/volume = 7.5 ft²/ft³.

Specimen SAE 1018.

Dynamic test per MIL-P-3420; SAE-1045 specimen.

Equilibration Time

Paper only

(Static) With Specimens*

Specimen Rusting in Following Tests:

Static Jar

External Cell

Data on VCI Paper (a)

0	4 to 72 hours	None (Table 3)	- - - - -
25 days	3-1/2 hours	- - - - -	Heavy
5 days	16 hours	- - - - -	Heavy
2 days	6 hours	Scatt. spots	Heavy
1 day	4 hours	Scatt. spots	Heavy
1 day	72 hours	None	Pass**
4 hours	1 hour	- - - - -	Heavy
0	6 hours	None	Pass**
0	16 hours	None	Pass*

Date on VCI Paper (c)

0	48 hours	One fail, one OK (Table 3)	---
0	72 hours	No rust (Table 3)	- - - - -
25 days	3-1/2 hours	- - - - -	Heavy
0	72 hours	Spots overall	Heavy
0	72 hours	Spots overall	- - - - -
0	96 hours	Spots overall	
0	96 hours	Spots overall	

Dynamic test per MIL-P-3420 on VCI Paper (c):

Blank 40% rust. Vapor 60% rust. Contact no rust.

* "Specimen equilibration time" refers to time in the presence of the specimen, prior to condensation. This period is static in static jar tests; with air circulation in external cell tests.

** One small spot.

static jar tests and external cell tests were run with varying times of package and specimen equilibration. When fresh (a) paper is put into a "package" and immediately equilibrated with the specimen in place, protection is obtained within about 4 to 6 hours whether the specimen is internal or external. When the "package" is assembled for one day with the paper only (no specimen), then the specimen must be present for an additional period before inhibition is obtained--this period is somewhere between 4 and 72 hours. When the "package" is assembled for 5 days and then the specimen is exposed to the package atmosphere for 16 hours, no protection was obtained. Although these data are not complete, they indicate that the (a) paper does not perform by establishing a rust-inhibitive atmosphere, but rather by actual transfer of inhibitor to metal surfaces. The external test cell method would seem somewhat difficult to apply to this paper; since in packages in storage for a year or more the transfer of inhibitor would be expected to be substantially complete, with a consequent deficiency of the inhibitor available in the atmosphere itself. It would appear that the internal specimen, assembled at the time of packaging, would be a more realistic indication of safe VCI level for this particular paper.

With regard to the data shown in Table 16 for the (c) paper, it is difficult to conclude anything except that the paper as of the time of test did not conform to MIL-P-3420. Earlier static jar tests had shown protection with 72 hours of specimen exposure. Three months later, tests under the same conditions showed failure. The (c) paper at this time also failed in an external cell test using a freshly-assembled package and 72 hours equilibration with the specimen. It also failed the standard MIL-P-3420 dynamic test at this time. These data may indicate that the paper has deteriorated in storage, although the normal precautions of dry storage and barrier wrap were observed. In any case, it appeared inadvisable to do further work on this paper sample.

At this point in the development, both internal and external-specimen methods had been worked out in preliminary detail, and their limitations had been explored to some extent. Further work on application of these methods was deferred until later (see Section IX). In the meantime, some work was performed in attempting to fix the minimum safe level for rust protection in terms of per cent VCI saturation, as described in the following Section VIII.

SECTION VIII

MINIMUM SAFE LEVEL OF VCI ATMOSPHERES

It would be desirable to know whether there is some "minimum safe level" of VCI materials in package atmospheres below which protection will not be given. If there is such a level for a given VCI material, then the running of rust inhibition tests with external specimens will have a real meaning. Further, if this minimum safe level is substantially below the saturation value, then it would appear possible to detect the approach of unsafe conditions which the actual VCI level was still above the minimum. This might be done if a minimum safe level could be established in terms of per cent VCI saturation; then a test procedure could be worked out using a predetermined dilution of a sample of the package atmosphere, so as to detect any substantial drop below the saturation value.

These considerations obviously apply only to VCI materials which consist of one single compound, or a group of closely related compounds, and which function through maintaining a rust-inhibiting atmosphere, rather than through transfer to the steel surfaces. It is felt that few of the currently available VCI materials meet all of these requirements, but the approach still appeared sufficiently attractive to warrant some work on it.

The equipment and the terminology for this work are somewhat different from those described in the preceding section. The tests on minimum safe level are carried out in gallon jars, which are used as a sort of test cell rather than as a "package". The VCI paper is cut into very small pieces and packed in a U-tube. Saturation of the atmosphere with VCI vapors is accomplished by circulating between the jar and the U-tube. For humidity control, it appeared most desirable to eliminate all aqueous solutions from the system because of possible absorption and release of the VCI vapors. Therefore, all original work was done in a controlled-humidity room at 50% R. H. For later work when it was necessary to operate at 80%, pre-equilibrations of the jar atmospheres and the diced paper (in separate operations) with constant-humidity solutions were used. These solutions were not employed after the jar and U-tube were connected for establishing VCI saturation of the atmosphere.

The steel specimens were again SAE-1018 rod, 3/8" x 4" or 3/8" x 6", and were finished as described in Section VII. For most of the later work, the ends were ground down to 3/16" diameter for 1/2" of their length; and this section was used as the test surface. The specimens were mounted in the rubber stoppers closing the jars in one of two ways. The "exposed" bars were mounted in final position with a 65-mm. aluminum funnel around their upper ends, and were thus exposed during VCI saturation periods. The "fresh" bars were inserted after the VCI saturation periods, by means of a steel tube mounted in the rubber stopper. This tube was closed by a small stopper in its lower end during the VCI saturation period; then the "fresh" bar could be inserted, driving out the small stopper. The fresh bar was held in place by rubber tubing which also held the funnel around the upper end of the bar. This assembly is shown in Figures 1 and 2.

A considerable amount of work was done in establishing the conditions necessary to form definite visible rust on "blanks" without VCI paper. It appears that at 50% R.H. there is simply not enough water vapor available in the air inside the jar to give heavy rusting when a fairly large test surface is exposed. The total amount of water vapor is about 0.04 grams, and the entire amount cannot be condensed. Various methods were tried for obtaining definite rusting on blanks; these included:

- (1) special specimen degreasing procedures,
- (2) use of dry ice coolant,

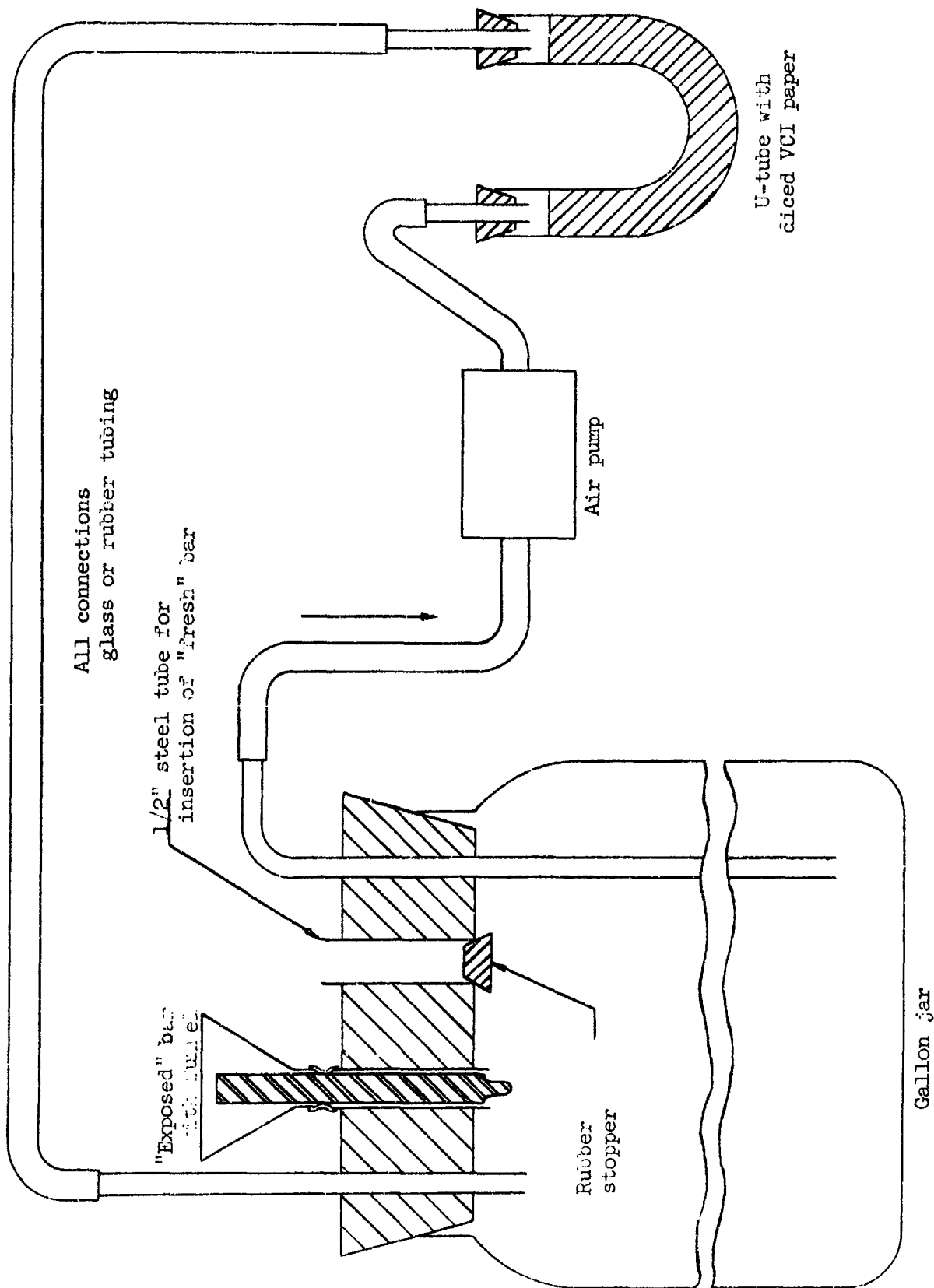


FIGURE 1
ASSEMBLY FOR ESTABLISHING VCI SATURATION

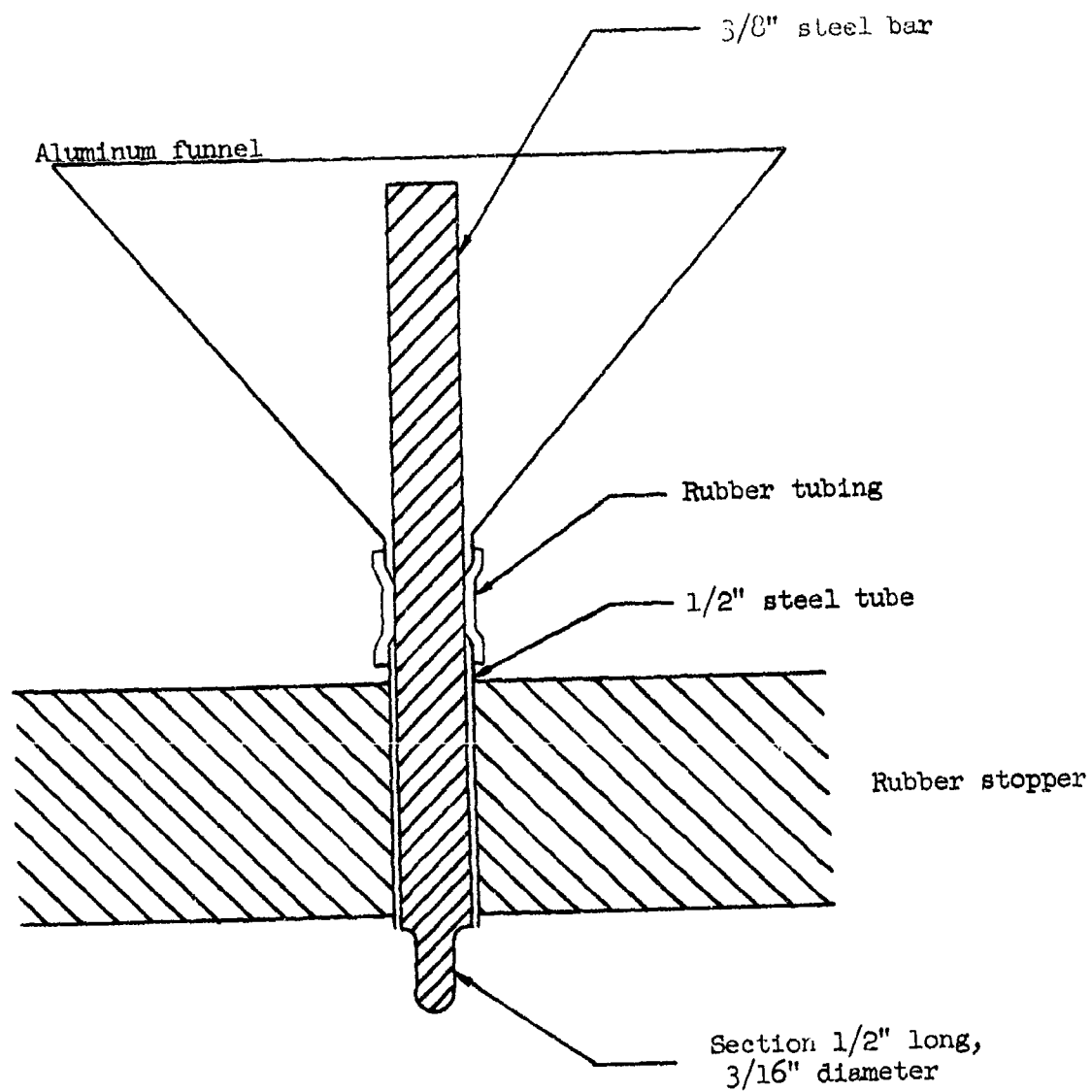


FIGURE 2
DETAIL OF INSERTED "FRESH" BAR

- (3) use of five-gallon jars as test cells to increase the total amount of water vapor,
- (4) addition of minute amounts of saturated calcium nitrate solution to supply additional water during condensation,
- (5) increase in condensation time,
- (6) increase in cooling efficiency by use of longer bars and larger funnels,
- (7) decrease in the section of the specimen exposed within the jar.

This work will not be described in detail; it is sufficient to say that (1), (2), and (3) were ineffective, and (4) is open to the objection previously stated as to possible absorption of VCI vapors. The conditions finally adopted were the use of ground-down sections $3/16'' \times 1/2''$ as the exposed portions of the specimens, and condensation times of 2 hours, with excess ice present in the water at all times. This apparatus and procedure gave definite and reproducible rust on blanks at 50% R.H.; but for present purposes the humidity was increased to 80% in studying the various VCI papers. As mentioned previously, this higher humidity was attained by pre-equilibrating the jar atmosphere and the VCI paper separately. The paper was stored over saturated ammonium chloride solution prior to dicing, while the jar atmosphere was circulated through a bubbler containing saturated ammonium chloride solution. Then the jar and the U-tube containing the diced VCI paper were connected and circulated to establish VCI saturation without the presence of any constant-humidity solution. It was assumed that three days of circulating at 80 in³/minute would be sufficient to establish VCI saturation in this type of apparatus, where air-paper contacts and circulation rates should favor rapid attainment of equilibrium. This flow rate corresponds to one complete pass of the air through the diced VCI paper in about 3 minutes, or about 1440 passes in 3 days.

The results of these tests on VCI papers (a), (b), (d), and (e) are given in Table 17. It can be seen that papers (b), (d), and (e) passed consistently; but (a) could not be made to pass at 80% R.H. even when using large excesses of fresh paper. At 50% R.H. (a) prevented condensation, and hence did not give a valid test.

In view of the poor results with (a) when attempting to pump the vapors and establish VCI saturation, the material was rechecked in a static jar test similar to that described in Table 5, using a SAE-1018 specimen and holding 50% R.H. with saturated calcium nitrate solution. Only 0.1 ml. of calcium nitrate solution was used here; and the size of paper used was reduced to 10 in² in one test, 20 in² in another. In each test perfect protection was obtained, which indicates that the (a) paper is effective under static conditions but is not amenable to pumping of its vapor from one place to another. This latter conclusion is in contradiction to that obtained from Table 16 data, in which the (a) paper did perform satisfactorily in an external test cell. All that can be said with certainty of the (a) paper is that its vapors are transferred with some difficulty, and that it does not appear advisable to use this paper in work on establishing minimum safe level without a knowledge of its mechanism.

It had been established, then, that the (b), (d), and (e) papers would produce a rust-inhibiting atmosphere by recirculating air over the diced paper. Further, for these papers there was evidently no significance to the "induction period" commonly thought necessary to establish some sort of adsorption equilibrium on the metal surfaces. It was noted that the fresh bars were protected just as well as the exposed bars, even in the case of (b), which had been demonstrated to be quite slow in action by previous work. Therefore, volatilization of the chemical and diffusion of the vapors must limit the speed of action of this paper, rather than any adsorption phenomena. These experimental facts may have a bearing on current theories of VCI mechanisms.

These three papers apparently functioned by means of establishing a certain vapor concentration which was sufficient to inhibit moisture as it condensed from that atmosphere. Therefore, it appeared logical to term these atmospheres "VCI-saturated", although the meaning of the term is questionable for certain papers in which vapor release depends on chemical reaction as well as on volatilization. At any rate, these "VCI-saturated" atmospheres were split to 50% VCI saturation by circulating the atmosphere of a VCI-saturated jar through another jar containing uninhibited air. This process was repeated to give 25% and 12½% VCI saturation. Jars containing these "partially-saturated" VCI atmospheres were then subjected to condensation of moisture on fresh and exposed bars as described previously. Data on these tests are listed in Table 18. It would appear from these results that the (d) paper has a minimum safe level below 12-1/2% of VCI saturation, while (b) and (e) have minimum safe levels between 25% and 50% VCI saturation. The data are questionable in that duplicate tests did not agree in several cases.

In addition to this type of information, the actual inhibitor concentrations at the minimum safe levels are of interest. Since the three VCI papers (b), (d), and (e) all contain nitrites, it appeared feasible to estimate the amount of such vapors present in a given volume of air by washing the air thoroughly with water, then determining nitrite in the water by conventional colorimetric methods. It should be noted, however, that in complex VCI systems the nitrite concentration in the air may bear no direct relationship to rust-inhibition. With this limitation in mind, data were obtained and expressed as milligrams of nitrite (NO_2^-) per cubic foot of air at test conditions.

Experimental:

In establishing the "VCI-saturated" atmospheres, the same procedure was followed as that described in Table 17--namely, the atmosphere of a gallon jar was circulated through a U-tube containing diced VCI paper for a minimum of 72 hours. In all tests reported herein, relative humidity was 80%. The test jar was brought to 80% by recirculating its atmosphere through an outside gas bubbler containing constant-humidity solution. The VCI paper was pre-equilibrated at 80% RH in a container with constant-humidity solution, removed for dicing, then transferred to the U-tube. The U-tube was connected to the gallon jar for the 72 hours or more of circulation. No constant-humidity solution was present in the system during this "saturation" period, since it was reasoned that such a solution would dissolve VCI from the atmosphere and retard VCI saturation of the atmosphere, or even reduce the ultimate equilibrium VCI concentration.

After "saturation" with VCI, the gallon jar was disconnected from the U-tube and connected to the bubbler containing 50 or 100 ml. of water. After recirculating the atmosphere for a minimum of 20 hours of bubbling through the water, absorption was considered complete. The water was analyzed for nitrite content by the well-known colorimetric determination of the reaction product of nitrite with sulfanilic acid and alpha-naphthylamine.

In case a 50%-saturated VCI atmosphere was to be tested by this procedure, the saturated atmosphere was circulated overnight or longer with another jar as described in Table 14; then one of these jars was hooked to a gas bubbler and circulated for nitrite absorption as described above.

The results of this work are listed in Table 19. When 50% VCI-saturated atmospheres were used, the nitrite concentrations were multiplied by 2 to put them on a

TABLE 17

RUST INHIBITION BY VCI-SATURATED ATMOSPHERE

Test No: 23-88, 23-89, 23-92
 Temperature: 25°C
 Humidity: 50% or 80%

Specimen: SAE-1018 steel rod, 3/8" x 6", with 1/2" length of lower end ground down to 3/16" diameter, Finished with #120 aluminum oxide cloth on all test surfaces.

Test Unit: One-gallon glass jar.

VCI Material: One square foot of paper, equilibrated at test humidity, then diced and placed in U-tube.

Specimen Location: "Exposed" bar in stopper in jar during equilibration. "Fresh" bar inserted through tube after equilibration period. See Figures 1 and 2.

Equilibration: Jar atmosphere pre-equilibrated at test humidity -- either by standing open in room for 50%, or by circulating through NH₄Cl solution for 80%. Jar atmosphere then circulated at 80 in³ minute through diced paper for 72 hours or additional periods as shown, with "exposed" specimen in place; no constant-humidity solution present.

Condensation: With jar static, "fresh" bar inserted and condensation induced immediately with wet ice in funnel; maintained 2 hours. After this bar became warm and dry the "exposed" bar was cooled similarly.

VCI Paper	% R. H.	% Rust		Remarks
		Fresh Bar	Exposed Bar	
(a)	50	No condensation obtained		
(b)	50	None	None	-----
(d)	50	None	None	-----
(e)	50	None	None	-----
(a)	80	50%	50%	
(b)	80	None	None	
(d)	80	None	None	
(e)	80	None	None	
(a)	80	80%	60%	Circulated air 5 days
(b)	80	None	None	"
(d)	80	None	None	"
(e)	80	None	None	"
(a)	80	----	15%	Circulated air 5 days, then installed fresh U-tube of (a), and circulated 3 days more
(a)	79	----	15% (2 tests)	Circulated 2+3+1 = 6 days with fresh (a) at start of each period.

TABLE 18

RUST INHIBITION BY
PARTIALLY-SATURATED VCI ATMOSPHERES

Test No.: 23-88, 23-89, 23-94
 Temperature: 25°C
 Humidity: 80%

Specimen and Assembly: As in Table 17

Equilibration: A "VCI-Saturated" jar, as described in Table 17, was circulated at 80 in³/minute with another jar containing non-inhibited air. These "50% VCI saturated" jars were split further by the same procedure to give 25% and 12-1/2% VCI saturation. No VCI paper or constant-humidity solution was used during these circulations.

Condensation: As in Table 17.

<u>% of VCI Saturation</u>	<u>VCI Paper</u>	<u>Test Number</u>	<u>Fresh Bar</u>	<u>Exposed Bar</u>
50%	(b)	1	No rust	No rust
	(d)	1	No rust	No rust
	(e)	1	No rust	No rust
25%	(b)	1	3% rust	10% light rust
		2	No rust	5% light rust
	(d)	1	No rust	No rust
		2	No rust	No rust
	(e)	1	3% rust	5% light rust
		2	No rust	5% light rust
12-1/2%	(b)	1	30% light rust	90% heavy rust
		2	One spot rust	No rust
	(d)	1	No rust	No rust
		2	No rust	No rust
	(e)	1	50% heavy rust	80% heavy rust
		2	60% heavy rust	90% heavy rust

TABLE 19
NITRITE ANALYSIS OF ATMOSPHERES

Test No. ****	VCI Satn. Time, Hours	% VCI Satn.	Water Wash Time, Hours	Ml. Wash Water	NO ₂ Absorbed from Atmosphere, mg/ft ³ , Calculated to 100% VCI satn.			Remarks
					(b)	(d)	(e)	
1	72	100	20	100	0.20	3.49	0.25	
2	72	100	40	100	0.60	3.41	0.65	
3	144	100	72	50	0.35	5.50	0.45	
4-i	168	50	24	50	0.10	0.10	0.40	(b) deposited crystals
ii			24	50	0.10	0.80	0.20	in Jar.
iii			24	50	0.07	0.48	0.10	(e) deposited film in
Total*	168	50	72	150	0.27	1.38	0.70	jar.
5-i	96	100	48	50	0.18	1.92	0.03	More efficient gas
ii			72	50	**	0.65	**	washing in absorber.***
Total	96	100	120	100	0.18	2.57	0.03	
6-i	96	100	72	50	0.15	1.45	0.10	More efficient gas
ii			72	50	0.10	0.20	**	washing. ***
Total*	96	100	144	100	0.25	1.65	0.10	Water adjusted to 9 pH before absorption.

* The VCI-containing atmosphere was circulated through single portions of water for periods shown; each portion of water was removed and analyzed separately.

** Not enough to determine.

*** Water in 25 x 300 mm. Test tube. Sintered glass disperser used.

**** Test No. 23-98, 101, 103, 106, 110, 112.

comparable basis with the data on full-saturated atmospheres.

It will be noted that the results were rather erratic; and it did not appear desirable to make further attempts within the scope of the contract to correlate atmospheric nitrite content with "minimum safe level" for rust prevention. However, it is pertinent to inquire as to the cause of the variation in nitrite results.

In the first place, it is noted that neither increasing the efficiency of the absorber as to gas contacting, nor adjusting the water to pH = 9 (to prevent possible HNO_2 decomposition) was effective in getting complete absorption by the first charge of water. The incomplete absorption possibly could be due to appreciable vapor pressure of the volatile nitrite, even from the dilute solution that results after absorption equilibrium is attained. This partitioning of nitrite between gas and liquid would depend on the volatility and water solubility of the particular nitrite involved, and could in principle be calculated from thermodynamic data. If this partitioning is of importance, then first-round absorption could be improved by using a larger volume of water in the absorber.

Another possible explanation of the incomplete first-round absorption is the adsorption of nitrite on the interior surfaces of the jar and accessory equipment. Making some entirely arbitrary calculations, based on 100 square Angstroms molecular cross-section for some unspecified nitrite, it is found that 0.1 mg. of NO_2 would cover as a monomolecular film 13,200 cm^2 , which is in the same order of magnitude as the total interior jar surface. In other words, a monomolecular film on this surface would contain as much nitrite as the air in the gallon jar would contain at $0.1 \times 7.5 = 0.75 \text{ mg/ft}^3$. Obviously, refined techniques would be necessary to determine whether adsorption plays any significant part in retarding the pickup of nitrite by the absorbing water.

Apart from the incomplete first-round absorption, there are other discrepancies observed. In the first place, it appears that test No. 4 should be eliminated from consideration. As noted in the table, both (b) and (e) showed definite deposits in their test jars. These deposits appeared during the VCI saturation period. Strangely enough, they did not disappear during the adjustment to "50% VCI saturation" by 72 hours' circulation to a second jar, nor did they disappear even in the subsequent 72 hours' circulation through the absorption cell. The only logical explanation for the deposits is poor temperature control in the constant-temperature room; or possibly local overheating of the air as it passed through the pump; and in either case it would have to be assumed that the crystal form of the deposits was such as to retard revolatilization during the subsequent processing. This argument may not bear close scrutiny, and it is preferable to eliminate test No. 23-106 from further discussion. An additional reason is the almost negligible nitrite picked up from (d) in the first-round absorption, contradicting all of the other test results on (d).

In considering the tests other than No. 4, certain regular variations become apparent. Tests 1, 2, and 3 show higher nitrite values than do 5 and 6, despite the two-stage absorption used in 5 and 6. This applies in practically all cases, the single exception being 1 (b). It is reasonable to ascribe these differences to variations in the water contents of the diced papers, which would in turn affect the true humidity during the "VCI saturation period". Although the papers were pre-equilibrated at 80% R.H., they were then removed

from the equilibration container and diced in the laboratory. In this process they would lose or possibly gain water according to the ambient humidity. The amount of water vapor in the gallon jar at 80% R.H. is only 69 milligrams, which is negligible compared to the amount of water introduced with the paper-- particularly where hygroscopic VCI's are involved. Therefore, it appears that the true humidity during the "VCI saturation" period is largely dependent on the condition of the paper at the time of assembly of the U-tube.

Assuming that the water content of the paper is subject to rather wide variations depending on atmospheric conditions, then it can be considered to effect nitrite volatilization in two ways. Any volatile compound will have a lower vapor pressure from water solution than it has in the pure state. Therefore, increasing wetness of the paper would be expected normally to reduce volatility. However, there would be an opposing tendency in the case of inhibitors which depend on chemical reaction among their components to release volatile nitrites. In such systems, increasing water contents are known to increase the rate of release of volatile nitrites, and hence would increase the observed atmospheric nitrite content.

Unfortunately it is not possible to check back on the test data to see which effect predominates. However, the theory does supply a reasonable explanation for the variations.

It is of some interest to compare the atmospheric nitrite content figures obtained here with vapor pressure determinations by other means. This would be of significance only when the inhibitor is a single chemical compound. It is found that vapor pressure values from the literature for one such compound are in the order of ten times higher than partial pressures calculated from "atmospheric nitrite content" data on the corresponding paper, even taking the highest values obtained here. This may indicate that appreciable water content or other factors inherent in the paper-inhibitor combination tend to reduce the vapor pressure markedly; or it may indicate a reduction in the rate of volatilization such that even the relatively long "saturation periods" used here failed to bring the inhibitor to true vapor equilibrium.

From the work done on atmospheric nitrite content, only two generalizations can be made. First, the (d) shows consistently higher atmospheric nitrite than (b) and (e). Second, the (b) shows less variation among tests than do the other two inhibitors.

It was of considerable theoretical interest to continue this type of work in an effort to eliminate the discrepancies by closer control of conditions. However, it became evident that rather refined techniques and considerable time would be required to answer the questions that had been raised. Furthermore, it is certainly not safe to assume that atmospheric nitrite content is related directly to rust-preventing activity for all nitrite-containing VCI's. The amount of work required to establish or deny the existence of such a relationship did not appear justified in view of the objective of this contract; therefore, all further work was directed at some of the more practical aspects of the application of the "package safety test".

This work on nitrite contents did serve to point out some of the refinements necessary as to humidity control in further work on establishing "saturated" VCI atmospheres.

SECTION IX

APPLICATION OF PACKAGE SAFETY TESTS TO INDICATION OF SAFE VCI LEVEL

In accordance with the stated objectives of this contract, it was desired to study the various test methods which had been developed as they might be used for the indication of safe level. Work on determining atmospheric nitrite contents had given erratic results. It is probable that the reproducibility of this type of test could be improved by changes in technique, but further work along this line appeared beyond the scope of the contract, particularly in view of the fact that not all of the currently qualified MIL-P-3420 materials contain nitrites. Therefore, in all subsequent work the formation of rust under condensation conditions was assumed to be the sole criterion of unsafe VCI level.

The possible types of tests that can be used on actual packages are as follows:

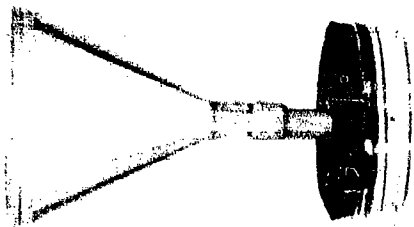
1. Internal specimens.
 - A. Specimen sealed in package when assembled.
 - B. Port designed in wall of package for insertion of specimen at time of testing for package safety.
2. External specimens--port designed in wall of package for insertion of probe for withdrawal of air from package to external test cell.

Method 1A appears to be satisfactory for all volatile rust inhibitors tested. Methods 1B and 2 are not satisfactory for paper (a), and may not be satisfactory for paper (c). The results on both of these papers have been somewhat contradictory, but most of the troubles encountered with them have come from difficulty in transferring a VCI-inhibited atmosphere through the test system. Therefore, it is assumed that in general the use of internal specimens, sealed in the package at the time of assembly, will show better protection for these materials and possibly will be more representative of their actual protective level in packages. This hypothesis has not been explored thoroughly due to time limitations.

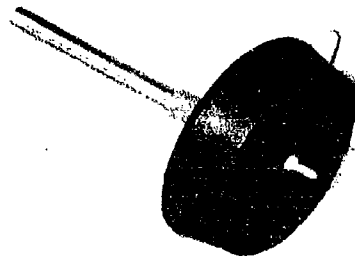
The external test cell appears to be easier to apply to actual packages, since the component to be designed as a part of the package would consist only of inlet and outlet connections for circulating air. Therefore, most of the work in application of test methods to indication of safe level was performed using external test cell.

Recommended Procedures

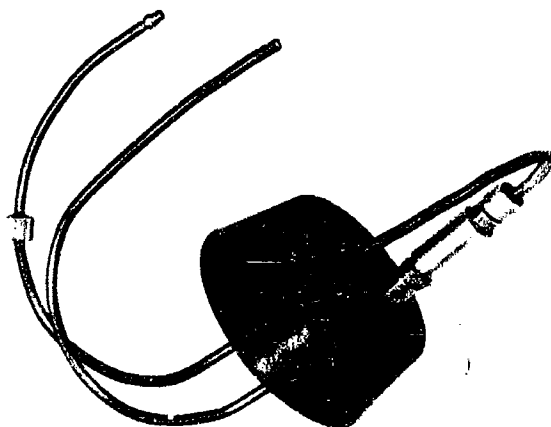
The assemblies as finally adopted for recommendation for packaging studies are shown in Figures 3 and 4. Details of the recommended methods are listed in Tables 20 and 21. It will be noted that for the internal specimen two alternate types of specimen have been recommended. The bar with ice water circulating through it has the advantage of better adaptability to varying package assemblies, since only the copper tubing connections go through the package wall itself. The bar specimen has the advantage of eliminating the need for an ice water pump, but may not be adaptable to all types of packages. Neither of these internal specimens will give an adequate test at low package humidities, so far as has been



GALLON JAR
SIMULATED PACKAGE
WITHOUT VCI PAPER



VIEW OF SPECIMEN
AND MOUNT
WITHOUT FUNNEL



ALTERNATE TYPE SPECIMEN
AND MOUNT WITH CONNECTIONS
FOR CIRCULATING ICE WATER

FIGURE 3
PACKAGE SAFETY TEST--INTERNAL SPECIMEN

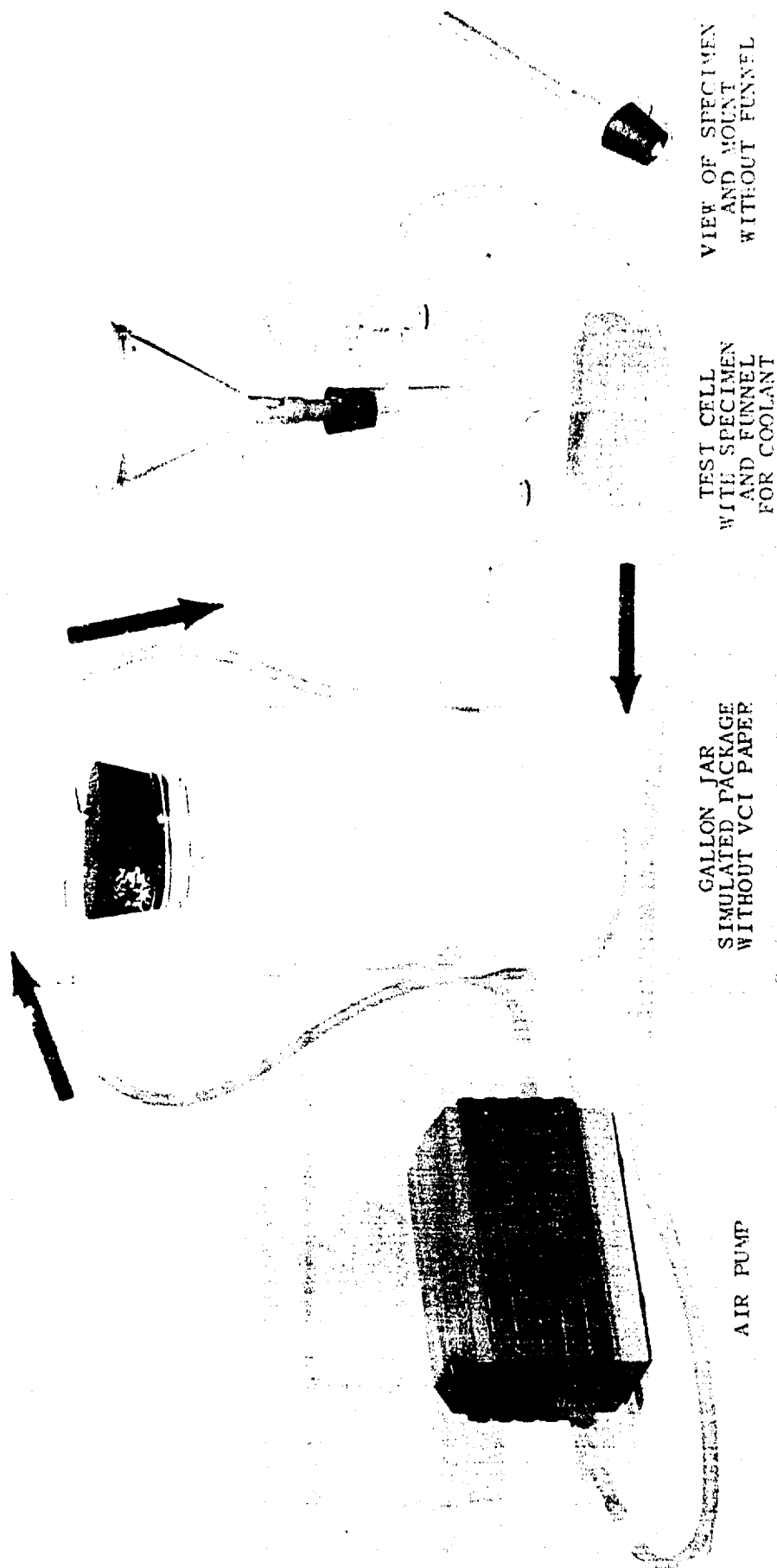


FIGURE 4
PACKAGE SAFETY TEST--EXTERNAL SPECIMEN

Table 20

TEST PROCEDURE
PACKAGE SAFETY TEST--INTERNAL SPECIMENS

Applicability: To all VCI Materials
Temperature: Ambient
Humidity: Ambient

Note: This procedure may not give valid results if the package atmosphere has a dew point below 14°C.

Package: Any type of package which can be fitted with a steel specimen and view window, and in which the specimen can be located in a representative position within the package.

Specimen: A round SAE-1018 steel rod, 3/8" x 6", with the critical test surface consisting of a 1/2" long section on one end, ground down to 3/16" diameter. Final grinding is with #120 aluminum oxide cloth, while the bars are turning at about 300 RPM. On the test surface, all edges and corners are well rounded. Abrasive dusts are removed by wiping with fresh gauze after grinding; but no degreasing procedure is used other than a preliminary naphtha wash before grinding.

Alternate Type Specimen: SAE-1018 steel rod 5/8" x 1", drilled and tapped for copper tubing connections for circulating ice water. Surface finish as above.

Specimen Mount: The specimen is mounted in a rubber stopper or it can be sealed into the package by any arrangement that will give an airtight seal with the 1/2" ground-down section in the package atmosphere. In any case, the mount must be such that the specimen can be inserted in the package without touching the critical test surfaces with hands, VCI materials, or any other contaminating object. A specimen mounted in a rubber stopper is shown in Figure 3.

Funnel Mount: A funnel with a neck that will just slip over the 3/8" specimen is mounted outside the package, sealing it to the specimen by means of a 1" length of rubber tubing. This tubing is slid down over the bar as far as possible; then the funnel is slipped over the upper end of the bar, and sealed into the top 1/4" of the rubber tubing. Dimensions of the funnel are approximately 3-1/2" diameter, 3" height, and 1/2" neck. The material of the funnel does not appear to be critical.

Procedure: The specimen must be mounted in the package at the time of packaging; the funnel can be mounted at any time. To test for package safety after a period of storage of the package, the funnel is filled with crushed ice and water. Excess ice is maintained in the mixture for two hours. It is necessary for a valid test that observable condensation be present on the critical test surface during this period. The specimen is then allowed to warm up, and is observed for rusting after one hour.

Interpretation: Any rusting of the critical test surface is an indication of unsafe VCI level in the package. The contact line of the specimen with the mount is not regarded as part of the critical test surface.

NOTE: No procedures are given for the alternate type specimen, since they have not been worked out in detail. The alternate type specimen is expected to give valid results at dew points somewhat below 14°C.

TABLE 21

TEST PROCEDURE
PACKAGE SAFETY TEST--EXTERNAL SPECIMENS

Applicability: To VCI materials which will furnish a rust-inhibitive concentration of vapors in the package atmosphere. Of the papers studied, the method is applicable to (b), (d) and (e).

Temperature: Ambient

Humidity: Ambient

Note: This procedure may not give valid results if the package atmosphere has a dew point below 6°C.

Package: Any type of package which can be fitted with an air inlet and outlet for circulating its atmosphere. The air inlet and outlet are blocked off when not in use. In circulation, the air should be drawn from a point in the package near ferrous parts needing protection and preferably not extremely close to VCI materials. The air should be returned to the package at a point as far away from the outlet as possible.

Test Cell: Glass test tube, 1" x 4", fitted with sidearm connections near bottom and top for air inlet and outlet. The air volume of the cell is 35 ml., not including connections, or about 45 ml. including all connections.

Specimen: Same as for internal-specimen test; see Table 20.

Specimen Mount: The specimen is inserted top end first, through a #4 rubber stopper, and positioned so that the 1/2" ground-down section shows below the stopper. The stopper is inserted in the test cell.

Funnel Mount: On specimen, as described in Table 20. See Figure 4 for details of external test cell assembly.

Air Pump: White Mist Model 50 (Haddaway Mfg.), modified by adding an air suction connection to permit recirculation. Air flow rate at free discharge is about 80 in³/minute.

Procedure: The package is connected to the air pump and test cell as illustrated in Figure 4. Air is circulated for one hour. Then the funnel is filled with crushed ice and water, and excess ice is maintained in the mixture for one hour, while air circulation is continued. Then air circulation is stopped and the cell is sealed off from the rest of the system. The ice is then dumped from the funnel, and the specimen allowed to warm up. The condensed moisture evaporates very slowly. The specimen is observed for rusting after one hour.

Interpretation: Any rusting of the critical test surface is an indication of unsafe VCI level in the package. The contact line of the specimen with the mount is not regarded as part of the critical test surface.

determined by test work performed under this contract. It is obvious that at dew points of 0°C. or below, wet ice cannot be used as the coolant; and attempts to use lower-temperature coolants for the internal specimens have not been very successful. In addition to these disadvantages, the internal specimens would require provision for view windows, or else the use of electrical methods for detecting initial rust.

The external test cells obviate most of these disadvantages, and are recommended for use with papers (b), (d), and (e). In addition, it appears that they will be satisfactory for powdered VCI's (f), (g), and (h).

Internal Specimens - Conditions for Rusting of Blanks. Tests were performed using the internal-specimen method essentially as described in Table 20, using end-cooled specimens. In these tests no VCI papers were used; the objective of the work was to establish conditions for obtaining adequate rusting of unprotected specimens at various humidities. The results of this work are shown in Table 22. It is apparent that at 50% or 90% R.H. there is no problem in obtaining adequate rusting of unprotected specimens with about 1 hour's condensation period using ice water. At 30 or 40% R.H., the results were erratic using ice water, with many of the tests showing no rusting even though condensation periods of 3 to 4-1/2 hours were used. Since 40% R.H. at 25°C. corresponds to a dew point of approximately 10°C., it is evident that difficulty was being encountered in cooling the lower end of the bar below 10°C., using wet ice on the upper end. By using dry ice coolant at -17°C. or -70°C., it was possible to condense observable water or frost on the lower end of the specimens at 30-40% R.H.; but again there were tests in which the rusting was not definite or heavy enough to serve as an adequate "blank". This is undoubtedly related to the previously-observed fact that visible rust forms very slowly at temperatures near or below freezing; it will form more rapidly during the warmup period while liquid water is still present on the specimens. At the lower humidities, this water evaporates rapidly, and may not allow time for visible rusting to occur.

These considerations appear to limit the usefulness of the internal specimen tests to packages whose atmospheres will have dew points of 14°C. or higher (corresponding to 50% R. H. at 25°C.). This limit may not be valid as applied to many actual packages, since it is expected that moisture-containing elements of the packages, such as paper, corrugated board, etc., would contribute substantial amounts of water vapor during the condensation cycle and probably permit adequate condensation at lower dew points than the 14°C. limit designated by these tests in glass containers. This theory would require proof, however.

This work and previous work on static jar tests have indicated many of the limitations of internal-specimen tests. All further work under this contract was directed toward evaluating external-specimen tests.

External Cells--Conditions for Rusting of Blanks
Using external cells by the method specified in Table 21, tests were run to determine the limits of applicability for adequate rusting of blank unprotected specimens. From previous work it appeared that humidities of 50% or above would present no problem in obtaining rust by using ice water as the coolant. Humidities of 30% and 40% at 25°C., or more generally, dew points of 6° to 10°C., are obviously more difficult to evaluate with wet ice. A series of tests were run at these lower humidities using external cells and "packages" consisting of half-pint, pint, and quart jars. The results on these blank tests are shown in Table 23. It can be seen that there are a few unexplained tests in which little or no rusting was achieved; but in general the amounts of rusting were sufficient to serve as adequate blanks.

TABLE 22

INTERNAL SPECIMEN TESTS
BLANKS AT VARIOUS HUMIDITIES

Test No.: 23-116

Temperature: 25°C

Humidity: 30-90%, as shown below, obtained by circulating atmosphere through outside bubbler containin g proper saturated salt solution, prior to starting test.

Specimen: SAE-1018 rod as described in Table 20.

Package: One-gallon glass jar.

VCI Material: NONE

Assembly and Procedure: As described in Table 20. Type of coolant and time of contact were varied as shown below.

Coolant		RH, %	Number of Tests	Condensation	Rusting
Temp., °C.	Time, Hours				
0-5	1	90%	2	Heavy	75% heavy
0-5	1-1/4	90%	3	Heavy	90% heavy
0-5	1	50%	2	Good	50% heavy or light
0-5	1-1/4	50%	3	Good	60-80% heavy
0-5	3	40%	3	Light	Erratic; from very light to heavy
0-5	4-1/2	40%	4	None	None
0-5	3	30%	4	One slight; others none	One 80% heavy; others none
0-5	4-1/2	30%	4	None	None
-17	4	40%	3	Good	One 50% light; others none
-17	4	30%	3	Good	70% medium to heavy
-70	4	40%	3	Frost	5-50% medium
-70	4	30%	3	Frost	50% medium

Temperatures nominally as shown.

0-5°C = ice-water

-17°C = dry ice-isopropanol (controlled)

-70°C = dry ice-isopropanol (excess dry ice)

TABLE 23

EXTERNAL CELL TESTS
BLANKS AT VARIOUS HUMIDITIES

Test No.: 23-122 to 23-136

Temperature: 25°C

Humidity: 30-50% as shown below, obtained by circulating atmosphere for 2 to 3 days through outside bubbler containing constant humidity solution as shown.

Package: Half-pint, pint, or quart jars.

VCI Material: NONE

Specimen: SAE-1018 rod as described in Table 21

Assembly and Procedure: As described in Table 21, except as indicated below.

Data shown below are in chronological order. Each rust rating is on duplicate tests.

RH	Coolant***	Schedule, Minutes			Rust Using Following		
		Circ.	Cool & Cool, Circ. Static		"Packages"		
					1/2 Pint	Pint	Quart
30%	CO ₂	60	22	0	Heavy	Heavy	Heavy
40%	Ice	60	35	0	Heavy	Trace	Light
50%	Ice	60	60	0	Light	Heavy, Trace	Medium, Trace

PUMPS AND ALL EQUIPMENT CLEANED

40%	Ice	60	15	5	Heavy, None	Heavy	Heavy
30%	Ice	60	60	150	Heavy	Heavy	Heavy, V. light
30%*	Ice	60	60	60	Heavy	Heavy	Heavy, Light
40%*	Ice	60	60	**	Heavy	Heavy	Heavy
30%*	Ice	120	60	60	Heavy	Heavy	Heavy, Light
40%*	Ice	90	60	60	Heavy	Heavy	Heavy, Light
30%*	Ice	120	60	60	Heavy	Heavy	Heavy

* These humidities obtained by glycerin-water solutions.

All earlier tests used saturated salt solutions.

** Coolant left in until ice was all melted, and warmup had been completed.

*** Dry ice or wet ice

When difficulties were encountered in the earlier tests shown in the table, they were thought to be due to pump contamination from previous work with VCI papers. However, dismantling and cleaning the pumps thoroughly, plus the usual cleaning procedures for all glass and rubber components, did not eliminate entirely the occasional test showing only light rusting. It appears logical to assume that the difficulty lies in the rather low dew points at which these tests are run (6 to 10°C.), which are so close to the minimum possible coolant temperature of 0°C. that minor variations in temperatures in the coolant or in the room itself can affect significantly the condensation conditions at the lower end of the bar.

All of this work was done in a room controlled at 25°C. \pm 1°C. and at a relative humidity of about 55%. In most of the earlier work shown in the table, the test cells were at the room humidity of 55% prior to connecting them with the "packages". In the extreme case, with a half-pint package at 30% R.H., this would result in raising the humidity of the system to about 34%. It is felt that variations of this small magnitude are not responsible for the occasional divergence or non-reproducibility of results.

This work on "blanks" with external cells has demonstrated that the method is applicable down to humidities of 30% at 25°C. (6°C. dew point), but the cause of the occasional discrepancies has not been proven definitely.

Minimum safe level by finalized procedures. After having established an external cell method, it was considered desirable to re-perform and extend some of the work done previously on minimum safe levels in terms of % VCI saturation, using finalized procedures as listed in Table 21. Also, certain precautions were observed in establishing humidities which had not been observed in earlier work on minimum safe levels.

In this new work, diced papers were placed in U-tube and equilibrated at the test humidity by recirculating air for at least 24 hours through the paper from a bubbler containing a glycerin-water mixture of the required proportions. The "packages" were brought separately to the test humidity by circulating their atmospheres through constant-humidity bubbles, for at least 24 hours. In most cases the external test cells were not pre-adjusted to the test humidity, since as discussed previously the change from nominal test humidity by such omission is only in the order of 4% in the most extreme case, and would be less than 1% for any of the work involving gallon jars as the packages.

After having equilibrated package and paper separately at the test humidity, they were then connected, and air was recirculated between them, with the pump drawing from the package and discharging through the U-tube containing the paper. This recirculation was continued for 3 days to establish nominal VCI saturation. In tests where partial VCI saturation was desired, the "saturated" jars were each connected to one or more pre-humidified jars of the same size, and air was recirculated through the jars to equalize the "VCI concentration" in the atmospheres of the jars.

After the desired level of VCI saturation was established, the jar to be tested was connected to a pump and external cell as shown in Figure 4, and the package safety test was run as described in Table 21.

Blank controls were run along with almost all of these tests, using pre-humidified jars without any VCI paper. It was found that heavily rusted blanks were

obtained in all tests, even at 30% R.H. This indicates that the method is sound, and that earlier discrepancies had been due to some unexplained difficulties in technique.

Data obtained on VCI papers (b), (d), and (e) using these methods, with half-pint jars as the packages, are listed in Table 24. It can be seen that there were a number of failures at relatively high VCI levels--at saturation with (b), and at half saturation with (e). Some of the failures occurred in tests in which the jar containing the VCI atmosphere stood overnight or longer before testing. This fact suggests that adsorption phenomena are involved; possibly some of the VCI becomes unavailable on standing, due to the establishment of adsorption equilibrium on the interior surfaces of the jar and stopper. There was only one failure observed using the (d) paper; and this occurred on a jar which had stood overnight at 1/4 VCI saturation.

In exploring this question further, tests were run with better control over the scheduling. The data are listed in Table 25. The relative humidity in these tests was 90% as compared to 30-40% in previous tests, but the results appear to be similar. It was found that when there is no time interval between cutting the VCI concentration and running the package safety test, then all three of the papers will protect at 1/2 to 1/4 VCI saturation. With a 2-hour interval between preparation and testing, only the (d) paper protected at 1/4 VCI saturation. With a 72-hour lapse, none of the three papers would protect. It seems reasonable to explain these data on the basis of an adsorption equilibrium which is established rather slowly; and conversely, it will not go in reverse rapidly during the performance of the package safety test. As indicated in Section VIII, the amounts of VCI in a monolayer on the interior surface of a gallon jar would be in the same order of magnitude as the vapor concentrations which had been determined by chemical analysis. Therefore, if such adsorption occurs, it would be expected to affect results significantly. This situation would be even more pronounced in the case of a smaller package such as the half-pint jar studied here, since the ratio of surface area to volume is greater in the smaller package.

Another group of tests shown in Table 25 also have a possible explanation based on adsorption equilibria. A VCI-saturated jar was circulated with three zero-VCI jars to give nominal 1/4-saturation. Then this original jar was circulated with another zero-VCI jar to give both a nominal 1/8-saturation. It was found that the original jar (as cut to 1/8-saturation) gave protection in the case of all three papers, whereas the fresh jar, also at nominal 1/8-saturation, did not protect in the case of the (b) or (e) papers. These results could be explained on the basis of the original jar having acquired a full load of adsorbed VCI during its circulation with the diced VCI paper. This adsorbed VCI might not desorb rapidly enough to distribute itself equally through all of the fresh jars in subsequent dilution operations, which ran about 1 hour each as compared with 72 hours for the original equilibration with the diced VCI paper. The net result would be a #1 jar which would have much more VCI than its nominal 1/8-saturation; and enough of this excess VCI might become available during the package safety test to afford protection at this low nominal VCI level.

The general conclusion from these data is about the same as that arrived at in Section VIII--that paper(d) is safe down to 1/8 VCI saturation or below, whereas (b) and (e) are safe down to 1/2 or 1/4 VCI saturation. The exact meaning of this conclusion is somewhat clouded by the lack of a fundamental definition of "VCI saturation" in terms of volatility and adsorption equilibrium.

All of this later work was done in half-pint "packages", which are thought to be about the minimum for the practical application of a package safety test, since

TABLE 24

MINIMUM SAFE VCI LEVELS
USING EXTERNAL CELL

Test No.: 23-137 to 23-141

Temperature: 25°C

Humidity: 30% or 40%; established by glycerin-water mixture.

Package: Half-pint jar

VCI material: One square foot, diced.

Equilibration: As described in text.

Package Safety Test: Procedure of Table 21.

VCI Material:	(b)	(d)	(e)	Blank
R. H., %	40%	30%	30%	30%

Rust in tests
at VCI satn. levels
as follows:

Satd.	None	None	None	Heavy
"	None	None		
"	10% V.Lt.	None		Heavy
"	3% V.Lt.	None		
1/2	None	None	50%	Heavy
"	None	None	75%	
1/2	None	None	75%	Heavy
"	40% Med.	None	None	
1/4	None	None	75% (1)	Heavy
"	None	None		
1/4	90% (2)	None (2)		Heavy
"	90% (2)	75% (2)		
1/4	None	None		Heavy
"	None	None		
1/8	90%	None	75%	Heavy
"	None	None	None	
1/8	None (3)	None (3)	75% (3)	Heavy
"	75% (3)	None (3)	75% (3)	

- (1) Jar stood overnight at 1/4 VCI saturation before testing.
- (2) Jar stood 3 days at 1/4 VCI saturation before testing.
- (3) Jar stood overnight at 1/4 VCI saturation before cutting to 1/8 saturation and testing. In each pair of tests shown, the first jar stood at 1/4 saturation; the second jar was a "zero VCI" jar, connected and circulated the next day to reduce both to a nominal 1/8 saturation.

TABLE 25

MINIMUM SAFE VCI LEVELS
USING EXTERNAL CELL

Test No.: 23-142

Temperature: 25°C

Humidity: 90%; established by glycerin-water mixture.

Package: Half-pint jar.

VCI Material: One square foot, diced.

Equilibration: As described in text. Unless otherwise indicated in table, each partially VCI-saturated jar was prepared not more than 2 hours before testing, by circulating a full-saturated jar with the required number of "zero-VCI" jars.

Package Safety Test: Procedure of Table 21.

VCI Satn.	Position of Jar *	Hours from Prepn. to Testing	Rust in Tests Using Following Papers:			
			(b)	(d)	(e)	Blank
1/2	1	0	None	None	None	Heavy
1/2	2	0	None	None	None	
1/4	1	0	None	None	None	Heavy
"	2	0	None	None	----	Heavy
"	3	72	75%	3 specks	----	
"	4	72	1 spot	50%	75%	
1/4	2	2	50%	None	25%	Heavy
"	4	2	50%	None	75%	
1/8	1**	0	None	None	None	Heavy
"	2	0	75%	None	75%	

* "position of jar" refers to the order of the jar in the series used for reducing VCI concentration from full saturation.

** The #1 jar in this series was originally at full VCI saturation. It was used in establishing a series of four "1/4-saturated" jars. Then, at nominal 1/4-saturation, it was circulated with still another fresh jar to obtain two 1/8-saturated jars.

smaller packages could be opened for inspection and repacked more readily than they could be tested indirectly. The general conclusions as to the minimum safe level were about the same whether half-pint or one-gallon packages were used, and it appears logical to extrapolate the results to larger packages.

A limited amount of work was done in studying the effect of specimen size on the results obtained in package safety tests. For this work, 1/2-saturated VCI atmospheres were prepared as described previously, and subjected to package safety tests using the regular specimen with the ground-down section, or straight 3/8" specimens. When using either specimen, about 1/2" of the end was actually in the test cell. As can be seen from the data, which are listed in Table 26, there did not appear to be any effect from the larger specimen--or at least any effect was overshadowed by differences between the #1 and #2 jars, presumably due to slow adsorption equilibria as discussed previously.

All of the work described in this section has pointed out that adsorption of VCI chemicals on all package surfaces must be considered in talking about the amount of chemical available for metal protection. However, the earlier conclusion still appear valid--that papers (b), (d), and (e) can establish a vapor concentration which gives a rust-inhibiting atmosphere. Therefore, the external specimen method is applicable to these papers.

Table 26

EXTERNAL CELLS
EFFECT OF SPECIMEN SIZE

Test No.: 23-143

Temperature: 25°C

Humidity: 90% (established with glycerin-water mixture).

Package: Half-pint or gallon jar as indicated below.

VCI Material: One square foot, diced.

Equilibration: As described in text. All jars were nominally 1/2-saturated with VCI, and were tested immediately after preparation.

Package Safety Test: External cell, procedure of Table 21. Specimens were either as described in Table 21, or a straight 3/8" bar without the ground-down section. The test surfaces of the two types of specimen had approximately the following areas:

Regular - 0.23 in²

Large - 0.53 in²

Jar Size	Position of Jar *	Specimen Area, in ²	Rust in Tests Using Following Papers			
			(b)	(d)	(e)	Blank
1/2-pint "	1	0.23	None	None	None	- - - -
	2	0.53	50%	25%	75%	- - - -
1/2-pint "	1	0.53	None	None	None	Heavy
	2	0.23	None	None	75%	Heavy
Gallon "	1	0.23	None	None	- - - -	Heavy
	2	0.53	None	None	- - - -	Heavy

* The #1 jar of each pair was originally at full VCI saturation.

It was circulated with a fresh jar (# 2) to obtain a nominal 1/2-saturation on both.

SECTION X

SUMMARY AND CONCLUSIONS

In the development of package safety tests, the use of rust inhibition as the criterion of safe VCI level has shown the most promise. Tests of this type using either internal or external specimens, and inducing condensation on the specimen, have been investigated thoroughly on a laboratory scale, and have been developed to the point of definite recommendations as outlined in Tables 20 and 21. Both methods are run at ambient temperature and humidity. Using wet ice as the coolant to induce condensation, there is a limitation of applicability under dry conditions. The internal-specimen method appears to be limited to dew points of 14°C. or above; and the external specimen method appears to be limited to dew points of 6°C. or above. The use of coolant temperatures below 0°C. is not an attractive means of removing this limitation, since rust formation is rather slow below freezing and the results of such tests are not reliable.

Apart from the limitation on dew point, the internal-specimen method appears to be applicable to all VCI materials. It has been studied under several conditions of humidity, but the effect of various package temperatures has not yet been studied. The principal disadvantage of the internal-specimen method is in the mechanics of its application, which is rather simple in laboratory simulated packages, but is expected to be rather complicated in actual packaging.

The external-specimen method eliminates most of the difficulties in application to packaging, since the components in the package itself are quite simple. The principal limitation of the external-specimen method is the reluctance of some of the currently-used VCI materials to be transferred from the package to the test cell by air flow. Of the five VCI papers tested, three can be tested successfully in external cells, and the other two are at best doubtful.

The principle behind both of these methods appears sound; and it is believed that rust-inhibition methods are the only practical approach to a package safety test. Therefore, both the internal and external specimen methods are recommended for further study in application to actual packages.

Several points of theoretical interest in the study of the mode of action of VCI materials have been discussed previously, and some of the conclusions will be repeated here.

The time required for inhibition of steel surfaces has been found to be three days or longer for some VCI papers. This time lag must be due either to slowness of diffusion of VCI chemical from the paper, or else to slowness of adsorption of the VCI chemical on the metal surfaces. Most of the data obtained under this contract indicate that slowness of diffusion of the VCI chemical is the principal factor in this delay. Once an atmosphere is established with an adequate concentration of VCI vapors, any fresh steel surface introduced into that atmosphere will be protected **instantly**. However, the time lag in establishing the adequate VCI concentration in the atmosphere can be rather great, particularly under static conditions. It is felt that this phenomenon could be of practical significance in packaging with VCI papers.

For some VCI papers, the mechanism of protection appears to be a transfer of chemical from paper to metal surface. For such papers, it is meaningless to refer to a rust-inhibiting concentration of vapors.

It is noted that high-sulfur steel is particularly difficult to protect against rust by most VCI materials. This suggests that other types of steels may likewise be more difficult to inhibit than the low-carbon steel which has been the criterion in most test work to date. More work on this subject would be desirable.

Several lines of approach to the problem of VCI mechanism have been suggested by the work performed under this contract. It is hoped that fundamental studies of VCI mechanism will be undertaken in the future, in addition to the immediate objective of application of the "package safety test" to actual packaging operations.

BIBLIOGRAPHY

A. VCI Materials

1. R. L. LeMar, Rock Island Arsenal Technical Report 53-3712, September 23, 1953. Volatile corrosion inhibitor bibliography.

Note: This Rock Island VCI bibliography is substantially complete through January or February 1953. Therefore, references listed therein are omitted here, with a few exceptions.

2. H. R. Baker, Naval Research Laboratory Report 4319, March 10, 1954. Volatile rust inhibitors.
3. A. A. Berk, U. S. Bur. Mines Report Investigation 3754 (1944) Amines check corrosion in condensate return lines.
4. T. Hayashi, Bull. Inst. Phys. Chem. Research Vol. 11, No. 12, p. 133. Reaction products between carbon dioxide and the organic base.
5. K. Akashi, Bull. Inst. Phys. Chem. Research. Vol. 12, No. 3, p. 22. Absorption of carbon dioxide by amine solutions.
6. D. C. Atkins, H. R. Baker, C. M. Murphy and W. A. Zisman, Ind. & Eng. Chem. 39, 491-7 (1947). Use of amine salts as inhibitors in synthetic oil.
7. E. G. Stroud and W. H. J. Vernon, J. of Applied Chem. 2, 166-172 (1952). Use of benzoates as inhibitors in packaging.
8. E. G. Stroud and W. H. S. Vernon, J. Applied Chem. 2, 178-184 (1952). Evaluation of amine carbonates as vapor phase inhibitors.
9. N. V. deBataafsche Petroleum Maatschappij, Dutch 71,374. Dec. 15, 1952. Nitrite salts of stable organic bases as corrosion inhibitors.
10. W. Weiler, Chem. Ztg. 76, 402-6 (1952). Corrosion proof packaging of machine parts and tools using vapor phase inhibitors.
11. A. C. Broyles (to Standard Oil Development.) U.S. 2,639,971, May 26, 1953. Volatile rust inhibition of air space corrosion in oil storage tanks.
12. P. F. deWinter, Chim Peintures 16, 215-8 (1953). Description of vapor phase inhibitors.
13. C. Jacklin, Corrosion 9 No. 7 Topic of the Month 1 (1953) Amines for Corrosion Prevention in steam condensate systems.
14. R. S. Wise, F. M. Watkins, et al, Corrosion 9, 151 (1953). List of Corrosion Inhibitors.
15. A. Wachter and N. Stillman (to Shell Development Co.) U. S. 2,643,176 June 23, 1953. Solid fibrous materials such as paper etc. impregnated with vapor phase inhibitors.

16. A. Wachter & N. Stillman (To Shell Development Co.) U. S. 2,643,177 June 23, 1953. Packaging methods using vapor phase inhibitors.
17. A. Wachter & N. Stillman (to Shell Development Co.) U. S. 2,643,178 June 23, 1953. Protection of Cu Alloys using amine nitrites plus ammonium carbonate.
18. C. H. Schaar (to Cromwell Paper Co.). U.S. 2,653,854, Sept. 29, 1953. Corrosion inhibiting packaging material and method of making.

B. Factors in Atmospheric Corrosion of Steel.

19. Iron and Steel Institute Special Report 1931 pg. 63-268. Gives partial results of the effect of variables on atmospheric corrosion.
20. Trans. Inst. Chem. Eng. 17, 171 (1939). Determined various factors affecting immersion and atmospheric corrosion.
21. J. C. Hudson, "The Corrosion of Iron and Steel" Van Nostrand, 1940 pg. 78. Weight losses of steel with different finishes upon outdoor exposure.
22. R. B. Mears & R. H. Brown. Ind & Eng. Chem. 33, No. 8 pg. 101 (1941). Discussion of causes of corrosion currents
23. F. L. LaQue, Alloy Constructional Sheets A.S.M. (1942) part 8 pgs. 140-205. Gives rate of weight loss with composition of steel.
24. W. H. J. Vernon, Chemistry and Industry 62, 314 (1943) Discusses the corrosion of steel.
25. C. P. Larrabee "Corrosion of Metals", ASM (1946) pgs. 30-50. Gives effect of composition and environment on corrosion of iron and steel.
26. J. J. Harwood & F. Schulman, Corrosion 5, 203-17 (1949) Corrosion research in the Navy.
27. G. Tolley, Metal Industries (London) 75, 89-91 (1949). Surface reactions of metals involving corrosion inhibitors.

C. Electrical Measurements in Corrosion Studies.

28. J. C. Hudson, Physical Soc. of London 40, 107-31 (1928). Method of measuring rust with resistance measurements.
29. J. Rutherford and R. Aborn, Trans. Am. Inst. Mining Met. Engrs. 100, 293 (1932). Resistance measurements of rusting iron wire.
30. F. J. Norton, JACS 61, 3162-68 (1939). A complex apparatus and circuit for measuring surface potential.
31. W. E. Shaw & D. L. Hawke, Org. Finishing 10, 19-22 No. 10, Change in resistance of surface due to breakdown of paint film.
32. Rosenfeld and Hoskins, Rev. Sci. Instrum. 16, 343-5 (1945). A highly complex circuit for determining surface potential.

33. M. Brotherton "Capacitors, Their Uses in Electric Circuits" - Brief description of various types of capacitors.
34. Meyerhof and Miller Rev. Sci. Instrum. 17, 15-17 (1946). A fairly simple way of measuring surface potential.
35. Joliet, C. R. Acad. Sci. Paris. 225, 1061-3 (1947). Very complex method of determining surface potential
36. J. Higuchi, Bull. Inst. Phys. Chem. Research (Tokyo.) 21, 1138-46 (1942) C. A. 42, 8556a (1948). Change in capacitance of condenser when iso-amyl alcohol was sorbed on silica gel packing.
37. D. C. Grahame, Phys. Rev. 72, 522 (1948). New techniques in the measurements of the capacity of the electrical double layer.
38. M. Thau, Am. Paint Journal 33, No. 49, 28-30 (1949). Uses of printed circuits in industry.
39. P. Van Rysselberghe, J. M. McGee, A. H. Gropp, R. D. Williams & P. Delahay, Corrosion 6, No. 3, 105-13 (1950). A polarographic examination of corrosion inhibition.
40. Mignolet, Disc. Faraday Soc. No. 8, 326-31 (1950), Method for measuring surface potential.
41. Mignolet, Disc. Faraday Soc. 105-114 (1950). Apparatus for Measuring surface potential.
42. Hackerman and Antes., Science 112, 471 (1950). Discussion of surface potential measurements.
43. Neuert and Hänsel, Z. Angew, Phys. 2, 319-23 (1950). Surface potential measurements.
44. Phillips, Sci. Instrum. 28, 342-7 (1951). Surface potential measurements.
45. F. K. Harris "Electrical Measurements" J. Wiley, New York, (1952). Discusses all types of electrical measurements.